



Co-metathesis of ethylene and olefinic compounds in ionic liquids

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Tungsten(VI) chloride dissolved in the ionic liquids is capable of catalyzing metathesis of 4-octene and co-metathesis of 4-penten-1-ol with ethylene; the latter reaction is preceded by double bond shift in the starting alkenol.

Low-temperature molten organic salts, *i.e.*, ionic liquids (ILs), can be used as the reaction media for diverse chemical processes, *e.g.*, metathesis of olefins. Recently metathesis of functionalized olefins in neutral ILs over ruthenium catalysts^{1–4} and metathesis of linear olefins in both neutral and acidic ILs catalyzed by tungsten compounds^{5,6} have been studied. In these works, general attention is paid to the homometathesis reaction in which two molecules of the same olefinic substrate interact. At the same time, metathesis in which two different olefins take part is of great interest.

The goal of the present work was the study of tungstencatalysed metathesis of diverse olefins with ethylene in ILs, the so-called ethenolysis. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆) were used as ILs, while 4-octene and 4-pentene-1-ol were chosen as olefinic compounds.[†] The catalyst was WCl₆ with tetrabutyltin additives, both compounds were predissolved in ILs prior to introducing 4-octene or 4-penten-1-ol in the reactor. Recently this catalyst has been used in metathesis of 1-hexene.⁵

Since ILs and 1-hexene are practically immiscible, the reaction proceeds at the interface of two phases.⁵ Additionally, metathesis

Table 1 Effect of duration of the reaction on the formation of olefinic pro-
ducts in ethenolysis of 4-octene (20°C; ethylene pressure, 60 atm; [bmim]BF ₄
WCl_6 as a catalyst, $SnBu_4$ as a promoter).

Time/h	Conversion of 4-octene (mol%)	Products, yield (mol%)			
		1-Pentene	3-Hexene	5-Decene	6-Dodecene
2	11.1	0.4	9.6	10.7	0.3
4	16.5	0.6	10.5	14.7	0.9
12	26.5	0.5	20.0	24.9	0.9
24	31.9	0.5	21.0	28.9	1.1

is accompanied by the double bond shift in the olefin molecule resulting in the formation of 2-hexene and 3-hexene, which also participate in the metathesis reaction.

Obviously, the double bond shift in initial 4-octene affords unsymmetrical olefins such as 3-octene and 2-octene. The distribution of the products can be used to recognize which reaction route for the chosen catalytic system is preferable: either ethenolysis or homometathesis of octene isomers (Table 1). Both the length and the double bond position depend on the nature of unsaturated hydrocarbon molecules taking part in the metathesis



* Synthesis of ionic liquids.

1-Butyl-3-methylimidazolium chloride ([bmim]Cl). A mixture of 0.3 mol of *N*-methylimidazole and 0.3 mol of butylchloride in an argon atmosphere was refluxed during 20 h on a water bath. The reaction product, [bmim]Cl, formed as a separate phase. The salt was washed by dry acetone $(3\times100 \text{ ml})$. A white solid (0.26 mol) was obtained in 86% yield.

 $[bmim]BF_4$. 0.25 mol of ammonium tetrafluoroborate (NH₄BF₄) was added in an argon atmosphere to 0.25 mol of [bmim]Cl in 120 ml of dry acetone. The reaction mixture was vigorously stirred at 20 °C for 72 h. The precipitate (NH₄Cl) was filtered off, and the solution of [bmim]BF₄ in acetone was evaporated in vacuum to give 0.21 mol of the IL (yield, 84%).

 $[bmim]PF_6$. 0.04 mol of [bmim]Cl was dissolved in 20 ml of water. Then 6.8 ml of 60% HPF₆ was added dropwise to the solution. The reaction mixture was vigorously stirred at 20 °C for 7 h. The reaction product

formed as a separate phase. The IL was washed with distilled water until the aqueous phase had a neutral pH value. The IL yield was 0.026 mol (65%).

Experiments on ethenolysis. The components (ILs, WCl₆, SnBu₄, 4-octene or 4-penten-1-ol in a molar ratio of 0.08:0.03:1:0.8) were loaded in a glass vessel. The vessel was placed in a copper cylinder to be sealed and was cooled at -30° C, then air was removed by the vacuum pump (5–10 Torr). Then the reactor was filled with ethylene, with controlling the pressure by gauge. During the experiment, the reaction mixture was vigorously stirred (20°C, the rotation speed 500–600 rpm). After the experiments, the pressure was reduced within 40–50 min, the vessel was cooled at 0°C and opened. Metathesis products were analyzed by GLC using two columns: the packed column 3 m×3 mm, SE-30 on Chromosorb (50°C); the capillary column 40 m, Porapack Q (50°C). For quantitative calculations of the product yields, the method of the internal standard was used.

 Table 2 Influence of the gas phase nature on the product composition.

Gas phase	Pressure/ atm	Conver- sion of 4-octene (mol%)	Products, yield (mol%)			
			1-Pentene	3-Hexene	5-Decene	6-Dodecene
$\overline{C_2H_4}$	28	31.9	0.6	22.0	28.9	1.1
N_2	27	8.5	0.1	5.7	7.7	0.3



Table 3 Dependence of the yields of the 4-penten-1-ol ethenolysis products on reaction conditions.

IL	Time/h	Pressure of	Substrate-to-catalyst molar ratio	Conversion of	Products, yield (mol%)	
		ethylene/atm		4-penten-1-ol (mol%)	Propenol	3-Buten-1-ol
[bmim]PF ₆	24	30	12:1	16.5	7.6	8.7
[bmim]PF ₆	24	60	12:1	33.7	15.8	17.4
[bmim]PF ₆	72	60	12:1	51.3	31.6	19.1
[bmim]BF ₄	24	60	12:1	13.8	5.7	7.8
[bmim]BF4	72	60	12:1	25.1	17.2	7.5
[bmim]BF ₄	72	60	3:1	80.1	73.8	5.9

reaction (Scheme 1). Indeed, 1-pentene, 1-butene and propylene can be produced from 4-octene, 3-octene and 2-octene, respectively.

Note that the main products are 5-decene and 3-hexene, both of them being formed in homometathesis of 3-octene, while the yields of the anticipated ethenolysis products are very low. Such a difference in the products yields can be explained as follows. The double bond shift in the formed 3-hexene results in 2-hexene, and further in 1-hexene. Homometathesis of the latter gives 5-decene. Alternatively, 2-hexene can take part in homometathesis to form starting 4-octene.

Evidently, the double bond shift also takes place in 1-pentene, which is the main product of the ethenolysis of 4-octene. 1-Hexene and 1-heptene are the products of ethenolysis of 3-octene and 2-octene and are detected in trace quantities. The double bond shift in 1-pentene should give 2-pentene which upon metathesis can produce 3-hexene. Small amounts of heptenes, nonenes, and undecenes being the products of co-metathesis of different olefins, were also detected in total yield no more than 0.1-0.2%.

Apparently, starting 4-octene can also undergo degenerate metathesis conversion, leading to the same 4-octene, and the reaction proceeding is invisible.

The data obtained show that ethylene reacts with octenes to a rather insignificant extent. This allows one to suppose that the use of an inert gas atmosphere (*e.g.*, nitrogen) instead of ethylene should not affect the 4-octene conversion as well as the composition of the reaction products. In order to check this suggestion, ethylene was replaced by dry nitrogen (Table 2).

The results indicated that the reaction proceeding in the nitrogen atmosphere led to a dramatic suppression of 4-octene conversion. The reason of such an unexpected result is a rather good ethylene solubility in the IL media, which, in turn, causes an increase in the solubility of higher olefins. As a result, the efficiency of the metathesis process increases as well.

It stems from these data that the rate of ethenolysis under the chosen conditions is very low, regardless of the fact that the presence of ethylene increases the 4-octene conversion. In this case, the main process is the homometathesis reaction in which general participants are olefins resulted from the double bond shift in octenes.

In order for the ethenolysis reaction to proceed, the substrate should be probably changed. For example, in the case of 4-penten-1-ol, homometathesis is suppressed by the influence of the hydroxyl group. The reaction between ethylene and this alkenol is apparently the degenerate metathesis. However, if the double bond shift reaction is the initial step of the process, then the ethenolysis can take place, and the products are 3-buten-1-ol and propenol (Scheme 2).

A number of runs with 4-penten-1-ol ethenolysis were carried out, differing in the nature of the ILs, as well as the pressure of ethylene, the substrate-to-catalyst ratio and the reaction duration (Table 3). The data obtained can be interpreted in the following way. In the beginning of the process, 3-buten-1-ol and propenol are formed in about equal amounts. Further the propenol yield becomes higher than that of 3-buten-1-ol. An extremely large difference can be achieved on increasing the catalyst-to-substrate ratio. This allows one to suggest that butenol is the intermediate product in the propenol formation, and the latter is the final reaction product. Furthermore, the double bond in propenol can be stabilized by interaction of the π -orbital with the electron pair of the hydroxyl oxygen.

It is worth to mention that the pentenol conversion depends almost linearly on the ethylene pressure in the system. It is also interesting that the homometathesis products are formed in small amounts under the chosen reaction conditions (their yields are less than 0.5%). The yields of the ethenolysis products are also influenced by the type of the IL.

Under the same conditions of ethenolysis, $[bmim]PF_6$ is more preferential than $[bmim]BF_4$.

In conclusion, neutral ILs such as $[bmim]PF_6$ and $[bmim]BF_4$ with dissolved WCl₆ (+SnBu₄) can be used as the reaction media in olefins metathesis and ethenolysis. The unsubstituted acyclic olefins participate in homometathesis and both the original olefin and its isomers formed through the step of the double bond shift can take part in the reaction. In the case of 4-penten-1-ol, ethenolysis is preferable, with the reaction products being 3-buten-1-ol and propenol.

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