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Metathesis of hex-1-ene in ionic liquids catalyzed by WCl_6

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Metathesis of hex-1-ene in ionic liquids catalyzed by WCl_6 was studied. The metathesis is preceded by isomerization of hex-1-ene to hex-2-ene, from which the main reaction product, *viz.*, oct-4-ene, is derived. The WCl_6—1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM \cdot BF_4$) system efficiently catalyzes metathesis of linear olefin, the ionic liquid serving as the reaction medium by forming a stable homogeneous catalytic system with WCl_6. The yields of the metathesis products increase with increasing reaction temperature. The addition of tin-containing promoters leads to a substantial increase in the reaction rate. In the WCl_6—$BMIM \cdot BF_4$—$SnBu_4$ system, the selectivity of the formation of oct-4-ene is significantly enhanced.

Key words: metathesis, ionic liquids, tungsten hexachloride, 1-butyl-3-methylimidazolium cation, hex-1-ene, oct-4-ene, isomerization.

Ionic liquids based on dialkyl-substituted imidazoles with the $AlCl_4^-$ and BF_4^- anions find use as solvents and catalysts for paraffin isomerization, Friedel—Crafts alkylation and acylation, nitration of aromatic hydrocarbons, Diels—Alder reactions, *etc.*[1] It was of interest to examine the possibility of performing such an important process as olefin metathesis in ionic liquids.[2,3] It should be noted that there are a few publications on metathesis in ionic liquids. In particular, metathesis of functionalized acyclic dienes with isolated double bonds in the presence of Ru alkylidene complexes (Grubbs catalysts)[4—7] and metathesis of pent-2-ene in the presence of tungsten-containing catalysts[8] was investigated.

The aim of the present study was to examine metathesis of hex-1-ene in the presence of WCl_6 as a catalyst. Ionic liquids based on the 1-butyl-3-methylimidazolium (BMIM) cation, *viz.*, neutral ($BMIM \cdot BF_4$ and $BMIM \cdot PF_6$) and acidic ($BMIM \cdot Cl—AlCl_3$, 1.0 : 1.05, and 1 : 2) systems, were used as the reaction medium.

$BMIM \cdot X^-$

$X^- = BF_4^-, PF_6^-, AlCl_4^-$

Particular attention was given to the acidic properties of the ionic liquids. The rates of side processes, such as the double bond migration, oligomerization, and polymerization of the starting olefin, would be expected to increase in acidic ionic liquids. Hence, it was of interest to examine the influence of the amount of aluminum chloride in ionic liquids on the ratio of the yields of the products of both the metathesis and side processes.

Experimental

Hex-1-ene, *N*-methylimidazole, $AlCl_3$, WCl_6, NH_4BF_4, Bu_4Sn, PPh_3, Bu_2SnO, $SnCl_4$, Ph_3SnCl, $SbCl_5$, and $SbCl_3$ were purchased from Aldrich, and $BMIM \cdot PF_6$ was purchased from Merck.

Preparation of ionic liquids

1-Butyl-3-methylimidazolium chloride (BMIM·Cl). A mixture of *N*-methylimidazole (0.3 mol) and butyl chloride (0.3 mol) was refluxed on a water bath under argon for 20 h. The reaction product was isolated as an individual phase. The resulting salt was washed with acetone (3×100 mL), and BMIM·Cl was isolated as a white crystalline substance in 86% yield (0.26 mol).

1-Butyl-3-methylimidazolium tetrafluoroborate ($BMIM \cdot BF_4$). Ammonium tetrafluoroborate (0.25 mol) was added to a solution of BMIM·Cl (0.25 mol) in anhydrous acetone (120 mL) under argon, and the reaction mixture was stirred at ~20 °C for 72 h. The precipitate (NH_4Cl) was filtered off. The solution of $BMIM \cdot BF_4$ in acetone was concentrated first on a rotary evaporator and then using an oil pump. The ionic liquid was obtained in 84% yield (0.21 mol).

1-Butyl-3-methylimidazolium tetrachloroaluminate ($BMIM \cdot Cl—AlCl_3$). Aluminum trichloride (0.114 mol) was added to BMIM·Cl (0.057 mol) during 3 h (for the 1 : 2 $BMIM \cdot Cl—AlCl_3$ system) or $AlCl_3$ (0.06 mol) was added during 2 h (for the 1 : 1.05 $BMIM \cdot Cl—AlCl_3$ system), the temperature of the reaction mixture being maintained at no higher than 25 °C. The ionic liquid was obtained in a yield of 0.57 mol. In both cases, the yield of the reaction product was 100%.

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Metathesis of hex-1-ene

General procedure. Experiments were carried out in a 15-cm^3 cylindrical reactor, which was preliminarily purged with nitrogen for 30 min. The components of the reaction mixture, *viz.*, a ionic liquid, a catalyst, hex-1-ene, and a promoter (in particular experiments), were placed in the reactor with continuous purging. The reactor was covered with a lid, which provided complete hermiticity of the reaction volume. Then the reaction mixture was vigorously stirred using a magnetic stirrer for a specified time (standard conditions: T = 20 °C, t = 1 h, the stirring rate was 500—600 rpm). After completion of the experiment, the reactor was cooled to 0 °C. Then a hydrocarbon layer was sampled under a stream of argon and analyzed by GLC.

The WCl_6—BMIM·BF_4 system. The catalyst (0.2 mmol, 0.08 g) and hex-1-ene (2.5 mmol, 0.3 mL) were added to the ionic liquid (2.0 mmol, 0.45 g).

Addition of a promoter to the WCl_6—BMIM·BF_4 system. The catalyst (0.2 mmol, 0.08 g), the promoter (0.07 mmol), and hex-1-ene (2.5 mmol, 0.3 mL) were added to the ionic liquid (2.0 mmol, 0.45 g).

The WCl_6—BMIM·PF_6 system. The catalyst (0.2 mmol, 0.08 g) and hex-1-ene (2.5 mmol, 0.3 mL) were added to the ionic liquid (2.0 mmol, 0.56 g).

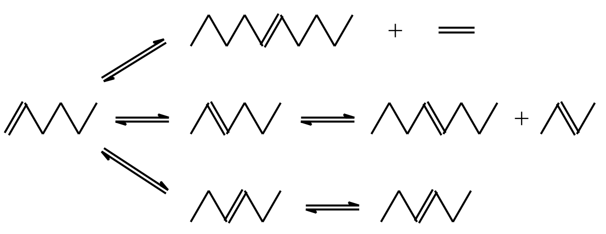
The WCl_6—BMIM·Cl—$AlCl_3$ system. The catalyst (0.2 mmol, 0.055 g) was added to the ionic liquid (2.0 mmol, 0.63 g) and the reaction mixture was stirred at 20 °C for 30 min. Then hex-1-ene (2.5 mmol, 0.3 mL) was added and the mixture was magnetically stirred for a specified time.

Analysis of the reaction products. The metathesis products were analyzed by GLC using packed (3 m × 3 mm, SE-30 on Chromosorb) and capillary (30 m, SE-30; 40 m, PEG-20M) columns. The yields of the metathesis products were determined by the internal standard method.

Results and Discussion

The experiments demonstrated that metathesis of hex-1-ene occurs in systems involving WCl_6 (Table 1). In most experiments, the reactions afforded oct-4-ene rather than dec-5-ene as the major product, in spite of the fact that the formation of the latter would be expected provided that the starting hex-1-ene enters into the reaction (Scheme 1).

Scheme 1



This situation can be attributable to the fact that isomerization of hex-1-ene to hex-2-ene proceeds much more rapidly than its metathesis. As a result, metathesis proceeds primarily with the involvement of hex-2-ene and, probably, hex-3-ene. However, in the latter case, degenerate metathesis can take place. According to the data published in the literature,[9] the concentrations of hex-1-ene, hex-2-ene, and hex-3-ene in an equilibrium mixture of isomers are 1, 66, and 33% at 20 °C and 2, 66, and 32%, respectively, at 50 °C (see Scheme 1). Actually, hex-2-ene and hex-3-ene were detected in small amounts in the final reaction mixture.

As can be seen from Table 1, metathesis proceeds in two catalytic systems, *viz.*, WCl_6—BMIM·BF_4 and WCl_6—BMIM·PF_6. The reactions with the use of these systems produced mixtures containing also small amounts of heptenes and nonenes (~0.2 and 0.1% yields, respectively), which are the co-metathesis products of different isomers of hexene. In the case of acidic ionic liquids containing the $AlCl_4^-$ anions, the main reaction pathway involves, apparently, oligomerization or even polymerization of hexene giving rise to resinous products. This

Table 1. Yields of the metathesis products of hex-1-ene in various catalytic systems[a]

Catalytic system	Conversion of hex-1-ene (%)	Yield[b] (mol.%)		Other products
		oct-4-ene	dec-5-ene	
WCl_6—BMIM·BF_4	12.8[c]	8.4	4.1	—
WCl_6—BMIM·PF_6	17.5	10.8	6.5	—
WCl_6—BMIM·Cl—$AlCl_3$ (1 : 1.05)	100.0	—	—	Resin
WCl_6—BMIM·Cl—$AlCl_3$ (1 : 2)	100.0	—	—	Resin

[a] Here and in Tables 2—4, the stoichiometry of the formation of ethylene and but-2-ene was maintained in all reactions.

[b] The accuracy of the determination of the yields of the metathesis products was 3—5 rel.%.

[c] In addition to the metathesis products, the reaction mixture contained small amounts of compounds formed in the side dimerization and oligomerization processes.

situation has been observed earlier.[10] In the reaction mixtures obtained in the experiments with the use of chloroaluminate systems, not only the products of metathesis, dimerization, and trimerization of the substrate but also hex-1-ene were absent.

Therefore, of all the systems under consideration, the WCl_6—BMIM • PF_6 system exhibits the highest activity in olefin metathesis. In this system, the upper liquid layer containing hex-1-ene turned dark-violet, which is characteristic of solutions of WCl_6 in olefins. It should be noted that the color of the ionic liquid layer remained unchanged, and a suspension of WCl_6 was visually observed in this layer. In the case of the WCl_6—BMIM • BF_4 system, the upper hex-1-ene layer initially also turned violet, but then the color disappeared. The ionic liquid layer formed a green homogeneous solution. Presumably, the catalyst in the former case is distributed between the hex-1-ene and ionic liquid layers and dissolves only in hex-1-ene. Apparently, the reaction in the WCl_6—BMIM • PF_4 system is the case of homogeneous catalysis of metathesis in the presence of WCl_6. By contrast, the reaction in the WCl_6—BMIM • BF_4 system proceeds at the interface of two liquids (homogeneous catalytic phase, *viz.*, catalyst—ionic liquid, and the olefin phase).

In another series of experiments, the olefin was replaced with a new portion of hex-1-ene within one hour after the beginning of the reaction. The results of these experiments are given in Table 2.

In the WCl_6—BMIM • PF_6 system, the total yield of the metathesis products after the replacement of the olefin decreases by a factor of two, the selectivity of the process being retained (see Table 2). Interestingly, after the replacement of the olefin, the hex-1-ene layer also turned dark-violet. Apparently, the ionic liquid BMIM • PF_6 plays an insignificant role as the medium for metathesis and serves as a diluent of the catalyst, thus preventing the latter from going completely into the hex-1-ene layer and forming no stable catalytic systems with WCl_6. In the case of the WCl_6—BMIM • BF_4 system, the hex-1-ene layer remains colorless after the addition of the second portion of the olefin, the yield of oct-4-ene remains virtually unchanged, whereas the yield of dec-5-ene decreases by a factor of ~2.5. Consequently, the selectivity of the formation of oct-4-ene increases, whereas the total yield of metathesis products decreases only slightly. Presumably, in this case, the already present active form of the catalyst interacts with the ionic liquid to form a stable homogeneous catalytic phase, which can provide olefin metathesis involving preliminary isomerization of hex-1-ene. A decrease in the conversion of hex-1-ene can be explained as follows. After the replacement of the olefin, the reaction proceeds at the interface, whereas, during the first hour, the reaction proceeds partially under conditions of homogeneous catalysis and partially under conditions of phase transfer catalysis.

Table 2. Characteristics of the reuse of catalytic systems in metathesis of hex-1-ene

Catalytic system	Time[a] /h	α[b] (%)	Yield (mol.%)		S[c] (%)
			oct-4-ene	dec-5-ene	
WCl_6—BMIM • PF_6	1	17.5	10.8	6.5	61.7
	2	8.7	5.3	3.1	60.9
WCl_6—BMIM • BF_4	1	12.8	8.4	4.2	65.6
	2	9.9	7.9	1.7	79.8

[a] Within one hour after the beginning of the reaction, the olefin was replaced with a new portion of hex-1-ene.

[b] Here and in Tables 3 and 4, the conversion of hex-1-ene.

[c] Here and in Tables 3 and 4, the selectivity with respect to oct-4-ene.

An increase in the temperature can influence not only the reaction rate but also the miscibility of two liquid phases. Hence, we carried out additional experiments at 50 °C. The results of these experiments are given in Table 3.

It appeared that the rise of the temperature from 20 to 50 °C has only a slight effect on the yield of the metathesis products in the WCl_6—BMIM • PF_6 system. In the case of the WCl_6—BMIM • BF_4 system, an analogous increase in the temperature leads to an increase in the yields of oct-4-ene and dec-5-ene by a factor of 2 and 1.5, respectively. This fact is attributable to an increase in miscibility of hex-1-ene and the ionic liquid with increasing temperature, and the viscosity of the ionic liquid therewith decreases. Both these factors exert a positive effect on the kinetics of metathesis. These results confirm the assumption that the WCl_6—BMIM • PF_6 system provides homogeneous catalysis of metathesis involving tungsten hexachloride, whereas the WCl_6—BMIM • BF_4 system provides phase transfer catalysis involving this homogeneous catalytic phase.

For both systems, we estimated the activation energies of the process (E_a). For the WCl_6—BMIM • PF_6

Table 3. Temperature dependence of the yields of the metathesis products

Catalytic system	T/°C	α (%)	Yield (mol.%)		S (%)
			oct-4-ene	dec-5-ene	
WCl_6—BMIM • PF_6	20	17.5	10.8	6.5	61.7
	35	19.5	12.5	6.8	64.1
	50	20.6	13.1	7.1	63.6
WCl_6—BMIM • BF_4	20	12.8	8.4	4.2	65.6
	35	19.8	14.2	4.7	71.7
	50	22.5	16.4	5.8	72.4

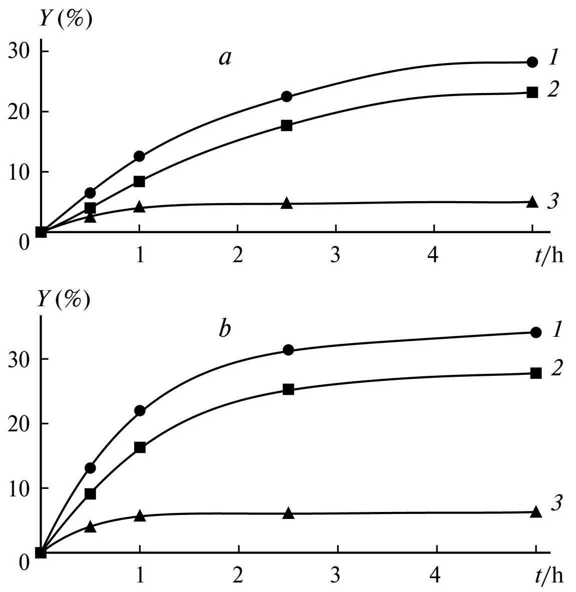


Fig. 1. Dependence of the yields of the metathesis products of hex-1-ene (*Y*) on the reaction time (*t*) at 20 (*a*) and 50 °C (*b*): the total yield (*1*), the yield of oct-4-ene (*2*), and the yield of dec-5-ene (*3*).

and WCl_6—BMIM • BF_4 systems, E_a are 4.4±0.2 and 15.1±0.2 kJ mol^{-1}, respectively. These results suggest that the pathway of the reaction involving the latter system, most likely, differs from that observed for homogeneous metathesis. Subsequent experiments were carried out for the WCl_6—BMIM • BF_4 system, which is most efficient in hexene metathesis.

It was of interest to elucidate how the yields of the products correlate with the thermodynamic equilibrium concentrations of the metathesis products. For this purpose, we performed experiments at 20 and 50 °C, in which the reaction time was varied.

As can be seen from Fig. 1, the yields of oct-4-ene and dec-5-ene were 23 and 5% at 20 °C and 28 and 6% at 50 °C, respectively, *i.e.*, the reaction performed at 20 °C for one hour produced the metathesis products, *viz.*, oct-4-ene and dec-5-ene, in 37 and 82% yields, respectively, of the maximum possible yields. An increase in the temperature to 50 °C led to an increase in both the reaction rate and the yields of the metathesis products. During 5 h, the total yield increased from 28 to 34% (28% for oct-4-ene and 6% for dec-5-ene, *i.e.*, after one hour the yields are 59 and 92% of the maximum values, respectively).

The yield of dec-5-ene in the WCl_6—BMIM • BF_4 system both at 20 and at 50 °C remains virtually unchanged with increasing reaction time, the maximum yield being obtained after one hour. This fact suggests that the major amount of hex-1-ene undergoes isomerization within one hour after the beginning of the reaction and then exclusively hex-2-ene is involved in metathesis.

Table 4. Influence of promoters on metathesis of hex-1-ene in the WCl_6—BMIM • BF_4 system

Promoter	α (%)	Yield (mol.%)		*S* (%)
		oct-4-ene	dec-5-ene	
—	12.8	8.4	4.1	65.6
Bu_4Sn	25.0	24.3	0.6	97.2
$SnCl_4$	23.8	18.8	4.8	78.9
$SbCl_5$	20.7	15.7	4.9	75.8
Ph_3SnCl	19.7	15.2	4.3	77.2
Bu_2SnO	18.8	14.5	4.2	77.1
$SbCl_3$	12.7	8.5	4.0	66.9
PPh_3	4.3	2.1	2.0	48.8

In modern catalytic systems for olefin metathesis, W, Re, or Mo-based catalysts are used together with tin-, lead-, antimony-, or aluminum-containing chlorides or organometallic compounds as promoters. To examine the effect of such promoters on the activity of the WCl_6—BMIM • BF_4 system, we carried out a series of experiments with Bu_4Sn, $SnCl_4$, $SbCl_5$, $SbCl_3$, Bu_2SnO, Ph_3SnCl, and Ph_3P as additives.

The results of these experiments (Table 4) demonstrated that Bu_4Sn is the most efficient promoter. It should be noted that the composition of the metathesis products obtained with the use of tetrabutyltin differs substantially from those obtained in the reactions with the use of all other compounds. In the presence of Bu_4Sn, the selectivity with respect to the metathesis products of hex-2-ene increases essentially (to ~98%). In the presence of other promoters, the selectivity with respect to oct-4-ene is substantially lower, and the yield of dec-5-ene is virtually the same (4—5%). Based on these data, it can be concluded that the addition of Bu_4Sn leads to rapid activation of the catalyst to form a complex soluble in the ionic liquid, and oct-4-ene appears in the ionic liquid medium, in which hex-1-ene undergoes isomerization to hex-2-ene.

The addition of triphenylphosphine sharply reduces the activity of the catalyst. The yields of oct-4-ene and dec-5-ene decrease by a factor of 4 and 2, respectively, which is, apparently, attributable to the fact that triphenylphosphine is involved in the coordination environment of tungsten and the resulting complex is inactive in metathesis reactions.

To summarize, we found that in WCl_6-containing ionic liquids, hex-1-ene undergoes isomerization to hex-2-ene, which is then subjected to metathesis. Of the catalysts under study, the WCl_6—BMIM • BF_4 system is most efficient in metathesis of hex-1-ene. In the latter case, the ionic liquid together with WCl_6 forms a stable homogeneous system, which acts under conditions of phase transfer catalysis. The addition of tetrabutyltin leads to an increase in the yield of metathesis products. In the

WCl_6—BMIM$\cdot$$BF_4$ system, the selectivity with respect to oct-4-ene increases to 98%.

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