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DFT Investigation into the Role of Conventional and Ionic Liquids as Solvents in Olefin Metathesis

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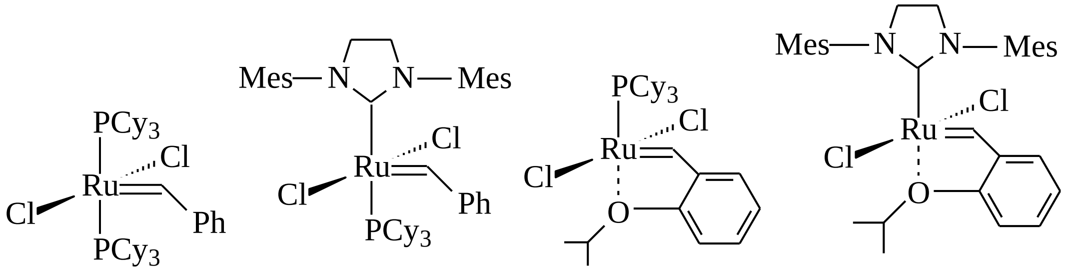
The effects of conventional and ionic liquids on the metathesis of olefin have been investigated by means of quantum chemical calculations to establish the factors favouring the metathesis of olefin in ionic liquid. The results suggest that ionic liquids stabilises olefin and the catalyst better than the conventional solvents. Ionic liquids also lower the activation energy more than the conventional solvents, leading to faster formation of the alkyledene intermediate. The equilibrium constant is higher for conventional solvents than for ionic liquids what suggests that conventional solvents have greater tendency to produce high yield than ionic liquid solvents.

Keywords: DFT, olefin metathesis, ionic liquids, conventional solvents, ruthenium alkylidene

1. INTRODUCTION

Olefin metathesis is considered to be an interesting carbon-carbon bond formation in which metal catalysed exchange of alkylidene moieties between alkenes occur even in presence of functional groups [1,2]. With the discovery of well-defined ruthenium catalysts (Scheme 1), olefin metathesis has resulted in their application in a variety of fields, from organic synthesis to polymer chemistry to biochemistry [3-7].



1 2 3 4

Mes = 2,4,6-methyl phenyl or mesityl: Cy = cyclohexyl

Scheme 1. Ruthenium catalysts

To overcome the problem associated with the cost of catalysts together with difficulties of final separation of the catalyst from the reaction medium and their subsequent recycling, several solutions have been explored. The immobilisation of Ru catalysts in non-conventional solvents such as ionic liquids [8-11], supercritical fluids [12-13] or perfluoroalkanes [14] are some among them. From the environmental point of view, the use of eco-friendly solvents in olefin metathesis is another important parameter to be considered. Various conventional solvents have been used in metathesis reactions; however, due to their toxic nature they have a negative impact on the environment [15-17]. In contrast, dialkyl carbonates are considered to be effective solvents in the metathesis reactions [18-22], particularly in the transformations of various renewable materials such as methyl oleate or terpenoids [23-25]. The use of ionic liquids as innovative medium for metathesis reactions has been receiving considerable attention [26-37]. Our previous work, discussing the experimental work on metathesis of methyl oleate and methyl ricinoleate in different solvents, it was shown that ionic liquids are better solvents than conventional organic solvents [36-37]. In this paper, density functional theory (DFT) method is utilised to understand the preference of ionic liquids as solvents for the metathesis of olefin.

2. EXPERIMENTAL

Chlorobenzene (PhCl), dichloromethane (DCM), 1,2-dichloroethane (DCE), toluene (PhMe), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF4]), 1-butyl-3-methylimidazolium bis (trifluoromethylsulphonyl)imide ([bmim][NTf2]) were all reagent grade from Sigma-Aldrich. Grubbs catalyst **1** was stored under N_2 and used as purchased from Sigma-Aldrich.

Geometry optimisations were done using the Density Functional Theory (DFT) method with the B3LYP functional and utilising the LanL2DZ basis set. DFT/B3LYP is considered adequate for providing information related to molecular reactivity [38]. The solvent effect was taken into account by utilising the Polarisable continuum model incorporated in the Gaussian program [39]. The dielectric constant for the ionic liquids [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] are 12.2, 11.8 and 14.0, respectively and were obtained from the studies by Huang *et al.* [40].

The solvent effect was calculated using the equation [41]

$G_{solution} = G_{vacuo} + \Delta G_{solv}$

where $\Delta G_{solv} = (E_{sol} + G_{nes}) - E_{vacuo}$

E_{sol} and E_{vacuo} are the electronic energy of the solute in solution and *in vacuo*, respectively and G_{nes} is the non-electrostatic contributions to the solvation free energy.

The activation energy of the forward reaction was estimated using the equation

$E_{act} = G_{inter-1} - (G_{react-1} + G_{react-2})$

where E_{act} is the activation energies for the forward and reverse reactions,

$G_{inter-1}$ is the free energy of the alkyledene intermediate,

$G_{react-1}$ is the free energy of the reactant 1 (olefin),

$G_{react-2}$ is the free energy of reactant 2 (the active catalyst),

G_{prod-1} is the free energy of the product 1 (styrene), and

G_{pod-2} is the free energy of the second product (the generated active catalyst).

The reaction enthalpy was calculated using the equation

$\Delta_r H = \Sigma\ H(\text{products}) - \Sigma\ H(\text{reactants})$

The nucleophilicity values were estimated as the inverse of the electrophilicity index value, with the electrophilicity index value being estimated from the equation [42]

$$\omega = \frac{\chi^2}{2\eta}$$

where $\chi \cong -\frac{1}{2}(E_{HOMO} + E_{LUMO})$ and $\eta \cong -\frac{1}{2}(E_{HOMO} - E_{LUMO})$

3. RESULTS AND DISCUSSION

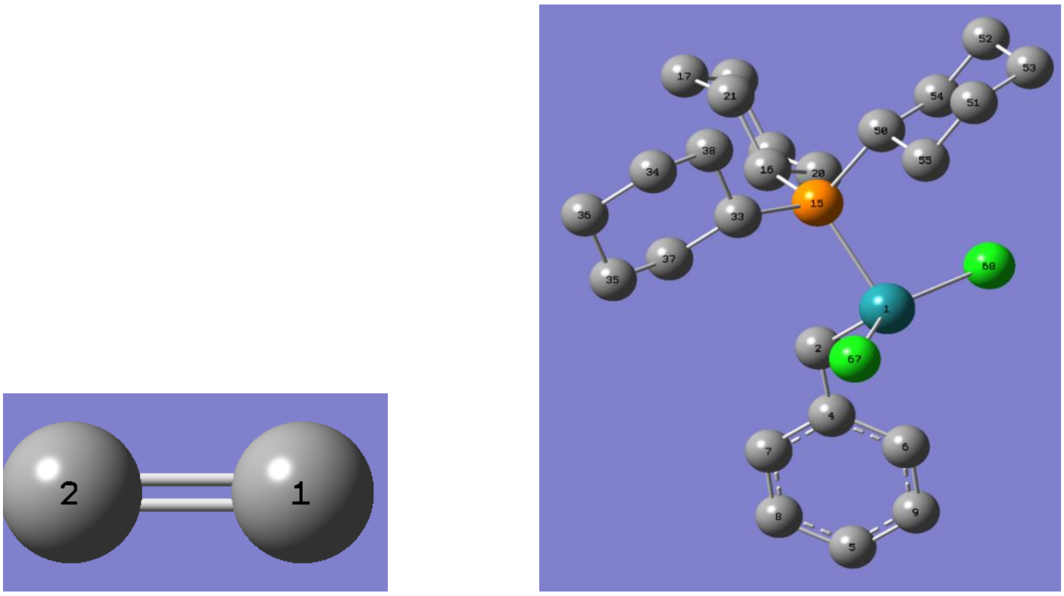
Various works have been reported in the literature regarding the mechanistic studies of Ru alkylidene catalysts in olefin metathesis. W.J. van Rensburg *et al*. [3] have reported the DFT studies of ethylene and Ru-methylidene as models for olefin substrate and alkylidene, respectively using Grubbs first and second generation catalyst. They have compared the basic mechanistic steps for olefin metathesis catalysed by Grubbs first and second generation catalysts as well as Phoban catalyst. DFT calculations were also employed in the mechanistic study of the reaction between 1-octene and Hoveyda-Grubbs second generation catalyst [4]. Recently, the electronic structures of 15 Hoveyda-Grubbs precatalysts have been analysed by DFT quantum chemical calculations [5]. To the best of our knowledge no modelling studies have yet been performed on studying the effect of solvents in the metathesis reactions.

Due to the high computational demand in studying large molecules, the study considers only ethylene, the simplest olefin, is considered with a view to explaining the preference of ionic liquids as solvents for the metathesis of olefins. Moreover, only the Grubbs first generation catalyst is considered and only the alkylidene intermediate is taken into consideration. The products of the metathesis are styrene and an active catalyst that could be used in the second circle of metathesis. To have a better understanding of the effects of the solvents, efforts were made to obtain the solvent effects (ΔG_{solv}) on olefin in order to establish their varying influence on the stabilisation of olefin. Information from the solvent effect (ΔG_{solv}) provides indication of the stabilisation extent of the solvent. Moreover, the activation energy, the equilibrium constant and the reaction rates in all the different media selected were determined in order to have an understanding of the effect of the solvent on these quantities. The solvents that result in lower values of reaction rate are better than solvent that results in higher reaction rates. Also solvents that results in high yield are better than solvents that results in low yields.

The three ionic liquids chosen include [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] and the four conventional solvents chosen include dichloromethane (DCM) 1,2 dichloroethane (DCE), toluene (PhMe) and chlorobenzene (PhCl). To determine the activation energy, the equilibrium constant and the reaction rate, optimisation calculations were performed in all the solvents followed by the calculations of the harmonic frequencies to obtain the free energy *in vacuo* and in different solvents.

3.1 Results in vacuo

The optimised geometries of the reactants, the intermediate (i.e., the metal alkylidene) and the products are shown in figure 1 to figure 3. Table 1 reveals the most interesting geometry parameters of the alkylidene intermediate. The shortest bond length corresponds to the C69-C72 while the longest bond length corresponds to the Ru-P bond. A comparison of the energy of the alkylidene (-1184.9684559) and the sum of the energy of the active catalyst (-1106.3794335 au) and olefin (-78.5782089 au) indicate that the alkylidene is 6.786 kcal/mol more stable than the sum of the isolated active catalyst and the olefin molecules.



Ethene active catalyst

Figure 1. The optimised geometries of the reactant molecules (ethene and the active catalyst). The blue atom is the ruthenium metal, the green atoms are the chlorine atoms, the orange atom is phosphorus and the grey atoms are the carbon atoms. The hydrogen atoms are not shown for simplicity sake.

Table 1. Selected geometric parameters of the alkylidene intermediate. *The numbering of the atoms is with respect to the numbering shown in Figure 2 for the alkylidene intermediate.*

Bond	Bond length (Å)	Bond angle	Bond angle
Ru-C2	1.871	C2RuP	92.5
Ru-P	2.514	C2RuCl67	33.4
Ru-Cl68	2.482	C2RuCl68	33.4
Ru-Cl67	2.472	C2RuC69	27.8
Ru-C69	2.372	PRuC69	14.8
C69-C72	1.379		

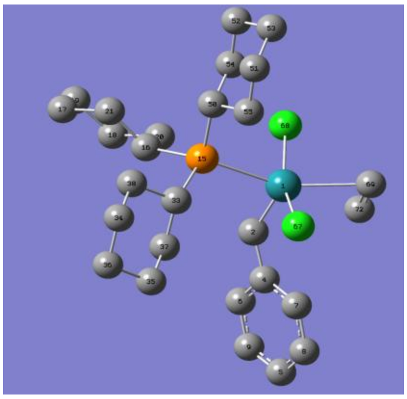
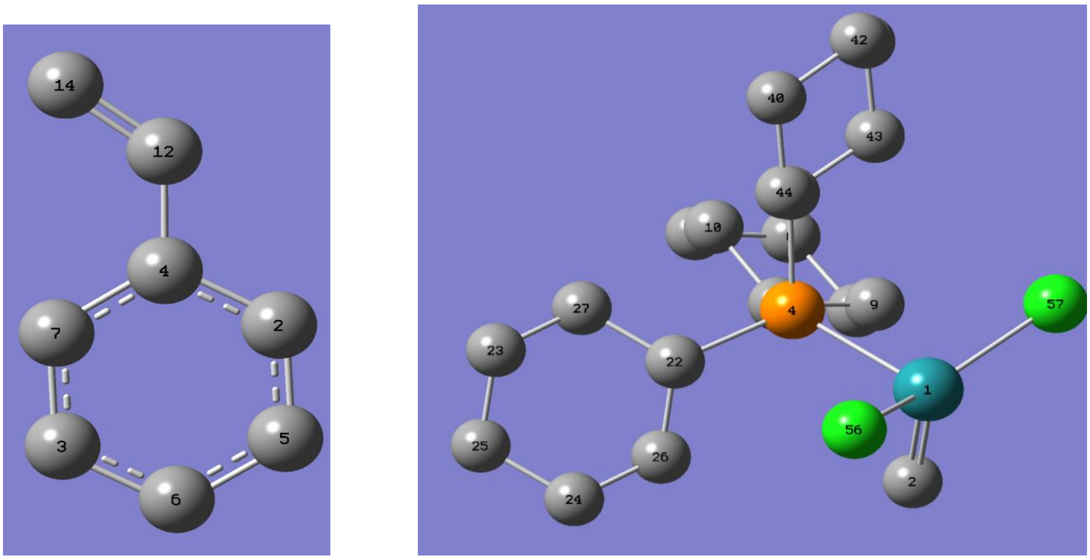


Figure 2. The optimised geometry of metal-alkylidene intermediate. The blue atom is the ruthenium metal, the green atoms are the chlorine atoms, the orange atom is phosphorus and the grey atoms are the carbon atoms. The hydrogen atoms are not shown for simplicity sake.



Styrene

the new active catalyst

Figure 3. The optimised geometries of the product (styrene) and the new active catalyst. The blue atom is the ruthenium metal, the green atoms are the chlorine atoms, the orange atom is phosphorus and the grey atoms are the carbon atoms. The hydrogen atoms are not shown for simplicity sake.

3.2 The bulk solvent effects

The solvent effects together with their components, the non-electrostatic ($G_{non\text{-}el}$) and electrostatic (G_{ele}) due to the different solvents on substrate (olefin, ethane) and the catalyst are shown in Table 2. For the purpose of illustrating the effects of the solvent on olefin metathesis, this work has been restricted to the determination of the metal-alkylidene intermediate and the styrene product.

The solvent effect is given by [46]:

$$\Delta G_{solv} = G_{el} + G_{cav} + G_{dis} + G_{rep}$$

where G_{cav}, G_{dis} and G_{rep} are the non-electrostatic contributions (cavitation, dispersion and repulsion contributions, respectively). Together G_{cav}, G_{dis} and G_{rep} are known as the non-electrostatic contributions to the solvent effect ($G_{non\text{-}el}$).

The results reveal that the olefin is strongly stabilised by non-electrostatic interactions, e.g., dispersion interactions. Moreover, non-electrostatic interactions are more predominant in the ionic liquids than in conventional solvents, which suggest that ionic liquids have greater tendency to stabilise olefin than conventional solvents. This result implies that olefin metathesis would preferentially occur in ionic liquids than in conventional solvents.

Table 2. Comparison of the solvent effect on the substrate and on the catalyst.

Solvent	solvent effect (ΔG_{solv})		
	ΔG_{solv}	G_{ele}	$G_{non\text{-}ele}$
Dichloromethane	1.74	-1.11	2.85
1,2 dichloroethane	2.13	-1.14	3.27
Chlorobenzene	2.65	-0.97	3.62
Toluene	2.30	-0.59	2.88
[bmim][BF_4]	3.71	-1.17	4.88
[bmim][PF_6]	3.72	-1.16	4.88
[bmim] [NTf_2]	3.68	-1.19	3.68

3.3 The role of the catalyst and the nucleophilicity of the solvent

Nucleophilicity gives information on the tendency of a molecule to donate electrons to the electron deficient centre of another molecule. It is understood that before the catalyst interacts with the substrate, it first undergoes a decomposition reaction forming an electrophile and is then considered active. It is at this stage that solvents have a strong influence on the catalyst. In the active form, the catalyst has a strong preference to react with more nucleophilic species. Therefore the solvent with greater nucleophilic character tends to bind strongly onto the catalyst, which makes the solvent less effective in olefin metathesis. Therefore understanding the nucleophilic character of the solvent provides information on the preferred solvent for the olefin metathesis.

The quantum parameters relevant for the estimation of the nucleophilic nature of the solvents are given in Table 3. The nucleophilic values (N_{nu}) of each solvent is given in the last column of Table 3. Since the ω value is the only relevant parameter for discussing the behaviour of the solvents towards the reactants, other parameters listed in Table 3 are hereby not discussed in detail. The order of nucleophilicity is such that DCM < DCE < PhCl < PhMe. This means that DCM has the least tendency to provide electrons to the cation and therefore, among the conventional solvents, would form the weakest bond with the cation. In contrast, PhMe has the highest tendency to donate electrons to the cation and therefore, among the conventional solvents, would form the strongest bond with the cation. Overall the order of reactivity in these solvents is such that PhMe < PhCl < DCE < DCM which agrees well with the experimental observations.

Table 3. Molecular properties of the ionic liquids [bmim][BF_4], [bmim][PF_6] and [bmim][NTf_2] and conventional solvents DCM, DCE, PhCl and PhMe calculated at B3LYP/6-31+G(d,p) *in vacuo*.

Solvent	Quantum chemical properties[a]						
	E_{HOMO}	E_{LUMO} (eV)	ΔE (eV)	η	σ	ω	N_{nu}
DCM	-8.422	-0.45	-7.972	3.986	0.251	2.468	0.405
DCE	-8.351	-0.185	-8.166	4.083	0.245	2.231	0.448
PhCl	-6.715	-0.366	-6.349	3.175	0.315	1.974	0.506
PhMe	-6.412	0.112	-6.524	3.262	0.307	1.521	0.657
[BMIM] BF_4	-7.818	-0.837	-6.981	3.491	0.287	2.683	0.373
[BMIM] PF_6	-8.463	-1.556	-6.907	3.453	0.290	3.633	0.275
[BMIM] NTf_2	-7.659	-1.721	-5.937	2.969	0.337	3.704	0.27

[a] *ω is the Electrophilicity index, N_{nu} is the nucleophilicity index, E_{HOMO} is the energy of the highest occupied molecular orbital (eV), E_{LUMO} is the energy of the lowest unoccupied molecular orbital (eV), ΔE (eV) is the energy difference between the HOMO and the LUMO, η is the global hardness and σ is the global softness values.*

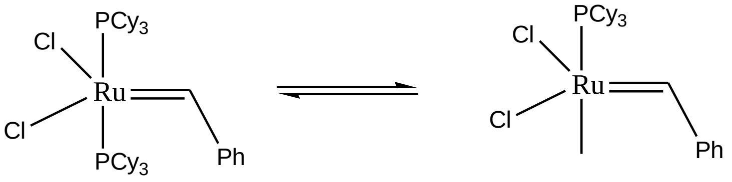
Among the ionic liquids, [bmim][BF_4] has the highest nucleophilicity while [bmim][NTf_2] has the lowest. However, overall, all ionic liquids have lower nucleophilicity than the conventional solvents, suggesting that ionic liquids have the least tendency to donate electrons to the active catalyst. Therefore ionic liquids would have weaker interactions with olefin than conventional solvents.

3.4 Transition state theory

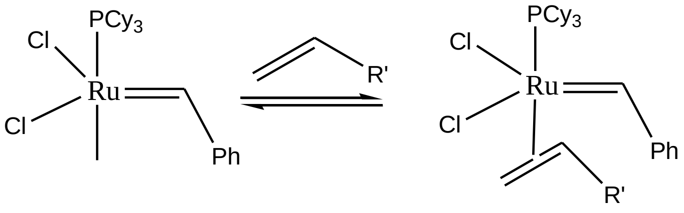
To better understand the factors involved in olefin metathesis, it is important to understand the theory explaining the reaction mechanism. One of such theories that is often used is the transition state theory. This theory considers that the reaction between one, two or more reactants, reaches the product state by passing over an activated complex. This activated complex is called a transition state. In the transition state theory, a potential surface is often assumed to connect the reactants, the transition state and the product. The transition state is the highest point (the maximum) on the potential surface and the rate of the reaction is related to the height of the barrier between the reactants and the transition state. In the metathesis reaction of propylene using W(0) complexes, density functional and Moller-

Plesset theory calculations show that the rate determining step of the metathesis is the initiation followed by the dissociation of olefin-metallocarbene complex [2].

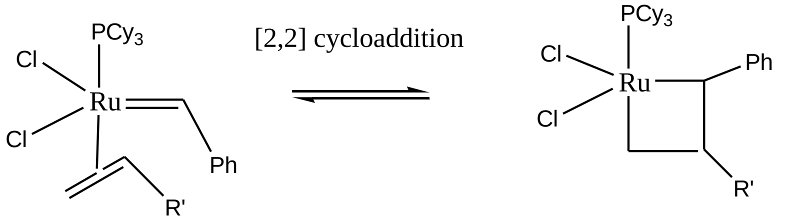
a) Generation of a vacant active site by elimination of PCy_3



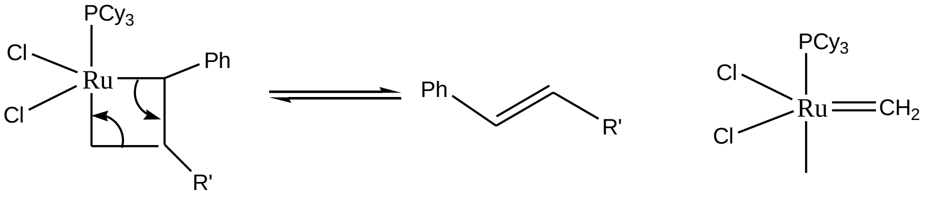
b) Coordination of olefin on the active site



c) The [2,2] cycloaddition reaction generating a metalocyclobutane



d) Metallocylobutane releases the propagating alkylidene species which continues to react with other olefin species in solution, effectively continuing the cycle



Scheme 2. Olefin metathesis reaction mechanism

3.4.1 The activation energy

Activation energy (ΔE_{act}) represents the energy change for a reaction in which a ground state is transformed into a transition state. It is also defined as the energy barrier for a reaction. A smaller value of ΔE_{act} for a reaction corresponds to a faster formation of the transition state. Solvent molecules influence the activation energy of reactions; a solvent with lower activation energy would lead to faster formation of the intermediate. A computational study done on the carbonyl containing olefins by Grubbs second generation catalyst demonstrates that the driving force of the metathesis reaction is the formation of a Ru–O coordination bond in the corresponding Ru acetoxyethylidene complex. The free activation energy of metathesis by the complex is higher than that of the metathesis reaction mediated by the conventional ruthenium alkylidene catalyst, due to the additional stabilization of the Ru center by a carbonyl oxygen revealing lower reactivity of carbonyl containing ruthenium carbene species [1].

In the current work, the activation energy in different solvents was estimated following the procedure discussed in the computational detail section. The results for the ΔE_{act} corresponding to the forward reaction are reported in Table 4. The results reveal that the presence of the solvent changes the activation energy. The lowest activation energy was obtained with ionic liquids. It was lower in DCM and DCE than in PhCl and PhMe. These results imply that ionic liquids give quicker formation of the intermediate.

Table 4. Activation energy E_{act} (kcal/mol) estimated from the free energies (kcal/mol) of the reactant and the intermediate. DFT/LanL2DZ calculations in different media.

Medium	Forward reaction			
	$G_{inter-1}$	$G_{react-1}$	$G_{react-2}$	E_{act-A}
Vacuum	-743211.284	-49290.255	-693928.788	7.759
Dichloromethane	-743558.604	-49306.791	-694245.479	-6.333
1,2 dichloroethane	-743556.381	-49306.405	-694242.993	-6.983
Chlorobenzene	-743552.51	-49305.885	-694238.879	-7.745
Toluene	-743553.207	-49306.234	-694238.551	-8.422
[bmim]BF4	-743548.897	-49304.826	-694240.358	-3.713
[bmim]PF6	-743548.823	-49304.82	-694240.24	-3.763
[bmim] NTf_2	-743549.182	-49304.849	-694240.811	-3.521

3.4.2 Equilibrium constant

The free energy change of the reaction in each medium may also be utilized to estimate the equilibrium constant for the process. Considering that the reactions were performed at room temperature, the equilibrium constant, $K_{eq,}$ may be estimated from the equation

$$\Delta G° = - RT\ln K_{eq}$$

which when rearranged can be written as

$$\ln K_{eq} = \frac{-\Delta G^0}{RT} \text{ or } K_{eq} = e^{\frac{-\Delta G^0}{RT}}$$

where R = 8.314 J mol^{-1} K^{-1} or 0.008314 kJ mol^{-1} K^{-1} and T is the temperature on the Kelvin scale.

The calculated equilibrium constant values are reported in Table 5. The results reveal that in all the solvents, $K_{eq} >> 0$ indicating that the presence of a solvent favours the formation of products. The highest yields corresponding to the largest value of K_{eq}, appear to correspond to reactions conducted in conventional solvents.

Table 5. The equilibrium constant and the rate constant for the metathesis of olefin in different media

Medium	K_{eq}	k_{TST} (s^{-1})
Vacuum	4.43×10^{-4}	5.69×10^{-10}
Dichloromethane	2.54×10^{6}	2.59×10^{-10}
1,2 dichloroethane	6.59×10^{6}	3.48×10^{-10}
Chlorobenzene	7.16×10^{6}	9.16×10^{-10}
Toluene	3.25×10^{6}	1.06×10^{-9}
[bmim]BF4	2.06×10^{6}	3.12×10^{-10}
[bmim]PF6	2.06×10^{6}	3.24×10^{-10}
[bmim] NTf_2	2.04×10^{6}	2.71×10^{-10}

3.5.3 Reaction rate

The transition state theory is also used to estimate the rate constant for a reaction from the following equation:

$$k_{TST} = (k_B T/h) \exp(-\Delta G^{\ddagger\circ}/RT)$$

where k_B and h are Boltzmann's and Planck's constants, respectively and $\Delta G^{\ddagger\circ}$ is the change in the standard Gibbs free energy between the transition state and reactants species (including the respective zero-point energies). The calculated reaction rate constants in different solvents are also reported in Table 5. The results reveal that the reaction rate in different solvents follows the order toluene > chlorobenzene > vacuo > 1,2-chloroethene > [bmim]PF_6 > [bmim]BF_4 > [bmim]NTf_2 > dichloromethane. These results imply that the metathesis reaction is favoured in organic solvents, which is in contrast to the trends observed from experimental data.

4. CONCLUSIONS

The effects of conventional and ionic liquids on the metathesis of olefin have been investigated by means of quantum chemical calculations to establish the factors favouring the metathesis of olefin in ionic liquid. The results suggest that ionic liquids stabilises olefin and the catalyst better than the conventional solvents. Ionic liquids also lower the activation energy more than do conventional solvents, leading to faster formation of the alkyledene intermediate. The equilibrium constant is higher for conventional solvents than for ionic liquids what suggests that conventional solvents have greater tendency to produce high yield than ionic liquid solvents.

The discrepancy in the values may be related to the incomplete consideration of the characteristics of the ionic liquids in the computation procedures. For the calculations in ionic liquids solvents, it is important to specify the 3-rank symmetric tensor representing the dielectric constant and the ionic strength in mol/dm^3 $Å^2$ [43]. However, these values were not readily, instead the calculations were performed only by specifying the dielectric constant for each ionic liquid. The dielectric constants were obtained from the work by Huang *et al* [40].

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