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High viscosity of ionic liquids causes rate retardation of Diels-Alder reactions

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Second order rate constants, k_2 have been determined for three bi-molecular Diels-Alder reactions to demonstrate that the high viscosity of ionic liquids can be a detrimental property in carrying out Diels-Alder reactions, if ionic liquids are employed as solvent media. It is possible to enhance the reaction rates of the reaction if a co-solvent is mixed in pure ionic liquid used as a solvent.

ionic liquids, viscosity, kinetics, Diels-Alder reactions

1 Introduction

The past few years have witnessed an increasing number of publications related to ionic liquids. Ionic liquid or room temperature ionic liquids have been considered as alternate solvents to the volatile organic compounds (VOCs) responsible for environment pollution. The interest in ionic liquids was initiated because of their advantageous physicochemical properties such as negligible vapor pressure, high thermal and electrochemical stability, high solvating power, etc. In the past decades, ionic liquids have been increasingly used for diverse applications such as organic synthesis, catalysis, electrochemical devices and solvent extraction of a variety of compounds in addition to many other areas [1–7].

While the advantages of ionic liquids are desirable, there exists a serious problem in handling these new materials. Ionic liquids possess high viscosity. This poses operational problems while making physical measurements and also carrying out reactions. High viscosity of these ionic liquids leads to the solvent friction that seems to determine the reactivity. It has been shown from our laboratory that the intermolecular Diels-Alder reaction between cyclopentadiene and acrylates is seriously hampered due to high viscosities of ionic liquids employed as solvent media [8]. In fact, these simple Diels-Alder reactions were faster in water than in any ionic liquids. It is important to note here that the role of viscosity in organic reactions has been a controversial issue. An initial increase in rates with increasing viscosity, contrary to the general expectation of deceleration due to viscosity, was reported several years ago [9]. These observations were explained on the basis of vibrational activation theory. On the other hand, it was asserted that the rates of organic reaction were independent of viscosity [10]. In an independent study, we observed a strong correlation between the retarding effects on the kinetics of the Diels-Alder reaction in the lithium perchlorate-diethyl ether (LPDE) medium and the high viscosity of the medium [11]. The LPDE solution above 5 M concentration showed a sudden decline, which was primarily due to the ~800% increase in viscosity beyond that composition. In another study from our laboratory, the reaction rates were noted to increase with the rise in viscosity, leveling off at 1.2–1.3 cP before dropping with increasing viscosity beyond 1.3 cP. This investigation was acknowledged for establishing the characteristic effects of frictional forces on reaction kinetics

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in conventional solvents [12].

Based on the limited data from the study of Diels-Alder reaction of cyclopentadiene with methyl acrylate, Welton had concluded that an increase in viscosity accelerated the Diels-Alder reactions [13]. Neta and coworkers acknowledged the role of the high viscosity of ionic liquids for diffusion-controlled reactions like elementary radical reactions in ionic liquids [14]. A study of the activation parameters of the bromination of alkynes in ionic liquids demonstrated that viscosity affected the rate of reaction by increasing the activation energy for bond breaking in the transition state [5].

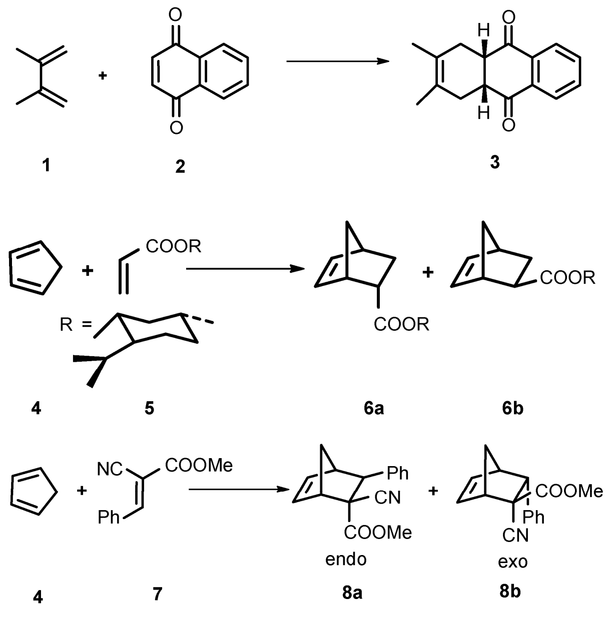
As a part of our ongoing research program on ionic liquids [15–18], we now present three Diels-Alder reactions (Schemes 1) in ionic liquids of varying viscosities with a view to understanding the effect of viscosity of ionic liquids on the kinetic profiles of reactions.

2 Experimental

2.1 Materials

2,3-Dimethylbutadiene **1,** 1,4-naphthoquinone **2**, cyclopentadiene **4**, (–) menthyl acrylate **5**, methyl (E)-α-cyanocinnamate **7** were either procured commercially or synthesized as reported [19]. Cyclopentadiene **1** was freshly cracked from dicyclopentadiene prior to its use. The purities of the materials were checked using ^{1}H NMR spectroscopy.

Ionic liquids used in the current investigations were synthesized by standard procedures. 1-ethyl-3-methyl tetraflouroborate [EMIM][BF$_4$], 1-butyl-3-methyl imidazolium tetraflouroborate [BMIM][BF$_4$], 1-butyl-3-methyl imidazolium hexaflourophosphate [BMIM][PF$_6$], 1-butyl-3-methyl imidazolium iodide [BMIM]I, 1-octyl-3-imidazolium hexaflourophosphate [OMIM][PF$_6$], 1-octyl, 3-methyl pyridinium tetraflouroborate [O3MPy][BF$_4$], 1-butyl pyridinium tetraflouroborate [BP][BF$_4$] and 4-methyl,1-butylpyridinium tetraflouroborate [4MBP][BF$_4$] were synthesized by the reported procedure [20–23]. The ionic liquids were thoroughly dried by heating at 70 °C under high vacuum for several hours before each kinetic run. The water content in all the ionic liquids as measured by Karl-Fisher coulometer was less than 50 ppm. The purity of ionic liquids was checked using ^{1}H NMR spectroscopy. All manipulations were carried out under an atmosphere of dry nitrogen to exclude moisture.



Scheme 1 The reactions of 2,3-dimethylbutadiene **1** with 1,4-naphthoquinone **2**, cyclopentadiene **4** with (–) menthyl acrylate **5** and **4** with methyl (E)-α-cyanocinnamate **7**.

2.2 Kinetic analysis

For a standard kinetic run, the dienophile was added to the ionic liquid (1 mmol in 1 mL of ionic liquid) and was allowed to equilibrate at the desired temperature. The temperature was controlled using a Julabo constant temperature bath at 298.15±0.01 K. The reaction was initiated by addition of **1** (1 mmol in 1 mL). The reaction progress was monitored at appropriate time intervals by extraction of aliquots with ether followed by appropriate dilution and GC analysis. The rate constants thus determined were reproducible to within 4%. A representative plot for the kinetic analysis is shown in Figure 1. The original references for understanding the reaction conditions for obtaining the kinetics of these reactions should be consulted. The rate constant k_2 was determined from the slope of the graph.

2.3 Viscosity measurement

The viscosity was measured using a cone and plate viscometer. The temperature was maintained at 298.15±0.01 °C with the help of a Julabo constant temperature bath. The viscosities thus measured were reproducible within ±3%. The viscosity measurements were carried out with the same

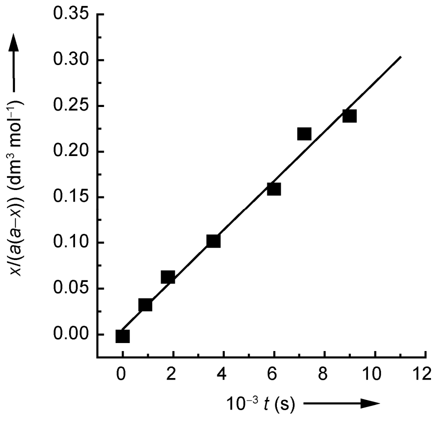


Figure 1 Plot of [$x/(a(a-x))$] against t for the reaction of **1** with **2** in [BMIM][BF$_4$] at 298.15 K.

sample of ionic liquids as used for the kinetic runs and at the same temperatures, in order to eliminate undesirable discrepancies.

3 Results and discussion

In order to investigate the effect of viscosity, several ionic liquids with graded viscosities were selected in which three Diels-Alder reactions were carried out. The investigated reactions were of 2,3-dimethylbutadiene **1** with 1,4-naphthoquinone **2,** cyclopentadiene **4** with (–) menthyl acrylate **5** and **4** with methyl (E)-α-cyanocinnamate **7** (Scheme 1). These reactions were selected on the basis of their kinetic data obtained in organic solvents as reported in the literature [24]. The second order rate constants, k_2 in organic solvents differed largely from each other thus offering us the test of the role of viscosity in a wide range of reaction rates. Similarly, the lowest viscosity of the ionic liquid selected for the study was as low as 20 cP for [EMIM][BF$_4$], and as high as 1000 cP for [BMIM]I providing us the range in which the kinetics could be examined. In Figure 2 are plotted the k_2 values for all the three reactions as a function of viscosity, η of eight ionic liquids. The viscosity values measured by our technique were [EMIM][BF$_4$] = 20.2, [BMIM][BF$_4$] = 92.1, [BMIM][PF$_6$] = 173, [BMIM]I = 1000, [OMIM][BF$_4$] = 600, [O3MPy][BF$_4$] = 668, [BP][BF$_4$] = 145 and [4MBP][BF$_4$] = 167 cP at 298 K.

The reaction of **4** with **7** is the fastest among the reactions studied, while the reaction of **1** with **2** is the slowest one. It is very interesting to note that the k_2 values in each case fall with an increase in the viscosity of ionic liquids. First, the reaction of **4** with **7** decreases very sharply in the ionic liquids possessing viscosities about 20 to 170 cP. Secondly, the k_2 value for this reaction in [BMIM]I is decreased by 50% when compared to in [EMIM][BF$_4$], while the viscosity increases from 20 to 1000 cP. This decrease in k_2 values for the reaction of **4** with **5** is about 3-times under identical conditions of viscosity. This observation is seen in all three reactions possessing the order of reactions from 10^{-5} to 10^{-3} dm^3 mol^{-1} s^{-1} carried out in the ionic liquids with viscosity ranging from about 20 to 2000 cP. This effect can be attributed to the presence of the encounter-controlled region in the high viscosity zones [12]. In this zone, the reactants cannot see each other due to diffusion problems resulting into the decline in the reaction rates.

Successful and effective application of ionic liquids as solvent media in organic transformations, extraction, electrochemical and microbiological processes require a precise knowledge of polarity of these compounds. Recently, our laboratory has contributed significantly to the measurement and understanding of polarity parameters of several ionic liquids [15, 16, 23, 25]. Since solvation is an important process during the reaction involving organic moieties, the polarity parameters of any solvent, including ionic liquids are expected to influence kinetic parameters of reactions.

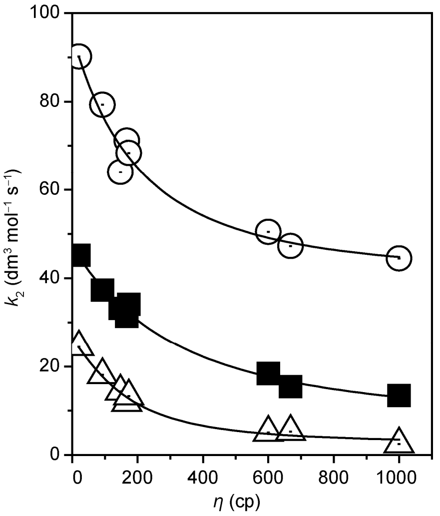


Figure 2 Second order rate constant k_2 as a function of viscosity η of the ionic liquids. (Δ) reaction of **1** + **2** with multiplication factor of 10^{-5} in k_2; (■) **4** + **5** with multiplication factor of 10^{-4} in k_2; (O) **4** + **7** with multiplication factor of 10^{-3} in k_2.

The polarity of many ionic liquids has been studied in terms of $E_T(30)$ (electronic transition energy in kcal/mol) and the Kamlet-Taft polarity parameters, α the hydrogen bond donor ability HBD: acidity, β the hydrogen bond acceptor ability HBA: basicity and π* polarizability. Though the kinetic parameters of these reactions cannot be correlated with accuracy using a multiple regression approach, the $E_T(30)$ and π* did not provide a correlation of rate constants with these polarity parameters. Similarly, surface tension data of ionic liquids do not correlate well with the rate constant values. Considering our previous reports and the fact that the rates were observed to be viscosity dependent, this lack of correlation was not very surprising. When a process is dominated by one of the solvent parameters governing the reaction, the effect of other variables, though present, tends to get "masked". In order to overcome this difficulty, the rate constant, k for the reaction in ionic liquids was corrected for its viscosity dependence to give a modified rate constant, k' as follows:

$$\ln k' = \ln B - a \ln \eta$$

With the above corrections, it is possible to fit the ln k' values with the help of the following correlation:

For the reaction **1** + **2**:

$$\ln k' = -11.3584 + 0.99\ (\pm 0.13)\ \alpha + 5.55\ (\pm 1.11)\ \beta + 15.28\ (\pm 3.46)\ \pi^* \quad (r^2 = 0.794)$$

For the reaction **4** + **5**:

$$\ln k' = -8.5282 + 0.82\ (\pm 0.09)\ \alpha + 4.87\ (\pm 0.98)\ \beta + 11.38\ (\pm 2.22)\ \pi^* \quad (r^2 = 0.914)$$

For the reaction **4** + **7**:

$$\ln k' = -4.5554 + 0.78\,(\pm 0.09)\,\alpha + 3.58\,(\pm 0.89)\,\beta + 11.33\,(\pm 2.88)\,\pi^* \quad (r^2 = 0.811)$$

The above correlations can be treated useful to correlate the rate constants of these three reactions. In Figure 3 are shown the correlated log $k'_{\rm cor}$ values against those obtained experimentally, log $k'_{\rm exp}$ confirming the utility of solvent parameters once the viscosity effects are considered.

Several years ago, we had demonstrated that high viscosity of molten organic salt, called tetra-n-butyl ammonium picrate can be significantly lowered upon addition of a solvent [26]. Recently, we carried out the similar experiment of adding a solvent in pure ionic liquid and observed a drastic reduction in the viscosity of pure ionic liquid [27]. This addition of a solvent has been called as a co-solvent, a solvent system that has been used in speeding up of the reactions. Using this experimental observation, we used such a solution of ionic liquid (mole fraction of [BMIM]I = 99.5% by weight with methanol as a co-solvent) for carrying out all the three reactions. The viscosity measured of [BMIM]I at this composition was 53 cP as compared to the pure one being 1000 cP. Surprisingly, the value of k_2 for the reactions of **1** with **2**, **4** with **5** and **4** with **7** were noted to be 12.3 × 10^{-5}, 45.3 × 10^{-4} and 179.2 × 10^{-3} $\rm dm^3\ mol^{-1}\ s^{-1}$, respectively. It is clear that addition of methanol as a co-solvent in a pure ionic liquid enhances the rate constants by approximately 5, 4.5 and 4 times for the reactions of **1** with **2**, **4** with **5** and **4** with **7**, respectively. These results demonstrate that addition of a co-solvent in pure ionic liquid, if employed as a solvent media for a Diels-Alder reaction.

4 Conclusions

We have demonstrated that it is important to examine the viscosity of ionic liquids before they are used as solvent media. The viscosity of ionic liquids can be lowered by adding a co-solvent in a very small quantity. This solvent medium when used for carrying out organic reactions can lead to high reaction rates. It is hoped that the attenuation of viscosity of viscous ionic liquids can be carried out with ease for carrying out the accelerated reactions.

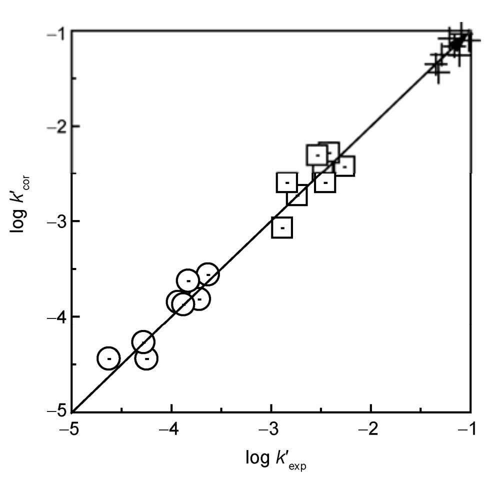


Figure 3 The plots of log $k'_{\rm cor}$ against log $k'_{\rm exp}$ for the reactions of (O) **1** + **2**; (□) **4** + **5**; (+) **4** + **7**.

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