Ionic Liquids

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Diels–Alder Reactions Are Faster in Water than in Ionic Liquids at Room Temperature**

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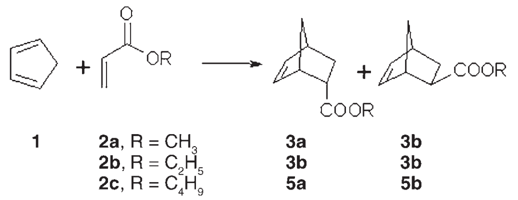
Over the past few years, there has been an increasing concern over the environmental effects of the use of volatile organic compounds as solvents. The quest for "green" solvents has led to the study of water, room-temperature ionic liquids (RTILs), and supercritical CO_2. Water, also known as nature's solvent, has been in focus after the pioneering work of Rideout and Breslow.[1,2] Meanwhile, much attention has been paid to the synthesis and characterization of RTILs and their use as solvents for carrying out organic reactions that are usually performed in organic solvents.[3] The advantages of using RTILs have been discussed in several reports.[4] Based on the studies made so far, the conclusion has been drawn that RTILs are highly effective in accelerating organic reactions, including Diels–Alder reactions.[5]

We demonstrate here that RTILs are not as effective as water in promoting Diels–Alder reactions. For this purpose, we have carried out three simple Diels–Alder reactions involving cyclopentadiene (**1**) with methyl acrylate (**2a**), ethyl acrylate (**2b**), and butyl acrylate (**2c**) (Scheme 1) both in water and RTILs (Figure 1) under identical conditions. In Table 1 are listed the second-order rate constants, k_2, for these reactions. The reaction of **1** with **2a** is ten times faster in water than in [BMIM]I. Similarly, rates of the reactions of **1** with **2b** and **2c** are at least three to four times higher in water than in [BMIM]I.



Scheme 1. Diels–Alder reactions studied in water and RTILs.

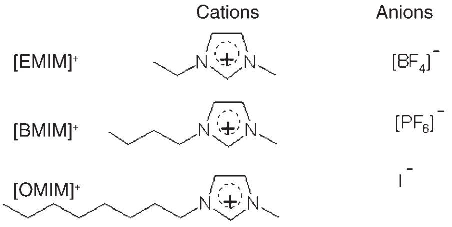


Figure 1. Structures of the RTILs used.

Table 1: Second-order rate constants (k_2) for Diels–Alder reactions in water and RTILs.[a]

Solvent	$k_2\,10^5$ [$dm^3\,mol^{-1}\,s^{-1}$][b] **1**+**2a**	**1**+**2b**	**1**+**2c**
water	24.1	7.9	5.7
[EMIM][BF_4]	5.9	5.7	5.2
[BMIM][BF_4]	4.5	3.9	3.4
[BMIM][PF_6]	3.9	3.3	3.1
[OMIM][PF_6]	3.1	2.4[c]	2.4
[BMIM]I	2.5	2.5[c]	2.1

[a] Reactions were carried out on a 1-mmol scale in 1 mL of solvent with a 1:1 ratio of the diene and dienophile at 298.15 K. The rate constants determined with 10 mM of **1** and 50 mM and 100 mM of **2a** agreed to within experimental error (±6%). [b] An average of three runs. [c] Values equal to within experimental error (±6%).

The experimental data present clear evidence that water can be a more powerful solvent than the ionic liquids, as far as Diels–Alder reactions are concerned. In the case of water, the rate enhancement has been ascribed to several factors, such as solvent polarity,[6a] hydrophobic packing,[1] hydrophobic hydration,[7] hydrogen bonding,[8] surface cohesive pressure,[2a,9] and surface tension.[2a,c] In general, the water-promoted Diels–Alder reactions can be better interpreted in terms of enforced hydrophobic hydration[7] and hydrogen bonding,[8] as discussed by Engberts and Jorgensen, respectively. The absence of hydrophobic interactions and weaker hydrogen bonding in RTILs may be important reasons for the observed difference in the rates between water and RTILs.

For the Diels–Alder reactions conducted in the RTILs, the rates drop by a factor of 2 on going from [EMIM][BF_4] to [BMIM]I. The trend is consistent for all three dienophiles studied, irrespective of the change in cation or anion. Thus the observed rate deceleration has to originate from a property that varies in a nonspecific fashion for all the RTILs used. An extensive examination of a range of properties was undertaken. Surface tensions[10d] of RTILs do not show any correlation with the reaction rates, as evident from such a comparison. The solvophobicity, $\delta_{11}(H^2)$, is also a weak correlating property in the case of RTILs.[5d] However, the rate constants of a Diels–Alder reaction carried out in different RTILs have been correlated with the H-bonding ability, expressed in terms of the E_T^{30} parameter.[5d] Our results support this correlation: the k_2 values of these reactions decrease with the decrease in E_T^{30} values of the RTILs.

The literature reports[10] suggest that the viscosities of different RTILs used in this investigation follow the order: water < [EMIM][BF_4] < [BMIM][BF_4] < [BMIM][PF_6] <

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[OMIM][PF$_6$] < [BMIM]I. Our preliminary investigation suggested that the k_2 values for these reactions decrease with the increase in the viscosity of RTILs. To provide tentative support for this observation, the reaction of **1** with **2a** was carried out at 298.15 K in a mixture of [BMIM][BF$_4$] with dichloromethane (DCM) (45 mol% of [BMIM][BF$_4$] in 55 mol% of DCM). Here, DCM ($\eta = \approx 18$ cP)[11] was used as a "viscosity reducer" for [BMIM][BF$_4$] ($\eta = 233$ cP). The resulting rate constant, $k_2 = 5.79 \times 10^{-5}$ dm^{3}mol^{-1}s^{-1}, is about 20% higher than that measured in pure [BMIM][BF$_4$]. It is, however, not possible to state at this stage with confidence that the viscosity of a RTIL is an important parameter to correlate kinetic data of Diels–Alder reactions. In a recent study with a series of RTILs, it was shown that the Diels–Alder reaction was fastest in the RTIL of highest viscosity.[5d] Inadequate experimental data do not allow us to draw any conclusion at this stage.

The results of preliminary temperature-dependent kinetic investigations are shown in Figure 2. The ΔH^{+} values for the reaction of **1** with **2a**, obtained from the transition-state theory plots (Figure 2), are 55.3 kJ mol^{-1} and 60.9 kJ mol^{-1} for [EMIM][BF$_4$] and [BMIM][PF$_6$], respectively. Any change in temperature is bound to alter both the H-bonding ability and the viscosity of RTILs. The observed temperature effect may result from a change in either or both these parameters. A detailed study of the theories of condensed-phase kinetics to explain the results is being carried out in our laboratory and will be reported in the future.

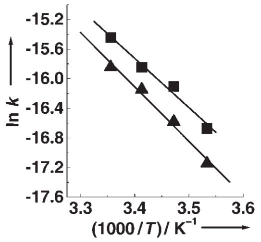

Figure 2. Eyring plots of Diels–Alder reaction of **1** + **2a** in [EMIM][BF$_4$] (■) ($r^2 = 0.991$) and [BMIM][PF$_6$] (▲) ($r^2 = 0.996$).

The present results indicate that water, and not a RTIL, is definitely the solvent of choice for carrying out Diels–Alder reactions. The results merit further investigation to correlate the rates of these reactions with other properties of RTILs. Also designing new RTILs or using RTIL mixtures with better properties is highly desirable in order to encourage their use as "green solvents".

Experimental Section

Cyclopentadiene (**1**) was freshly distilled from dicyclopentadiene prior to use. Acrylates **2a**, **2b** (low-pressure distillation), and **2c** were distilled prior to use. 1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$], 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF$_6$], 1-butyl-3-methylimidazolium iodide [BMIM]I, 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM][BF$_4$] and 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF$_4$] were synthesized by the reported procedure.[8a] The RTILs were thoroughly dried by heating at 70°C under high vacuum for several hours before each kinetic run. All manipulations were carried out under an atmosphere of dry nitrogen to exclude moisture.

Kinetic analysis: In a standard kinetic run the dienophile was added to the ionic liquid (1 mmol in 1 mL of ionic liquid), and the reaction mixture was allowed to equilibrate at the desired temperature. The temperature was controlled using a Julabo constant-temperature bath with an accuracy of ±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. (Varian CP-3800 gas chromatograph; for details, see the Supporting Information). The rate constants thus determined were reproducible to within 6%.

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