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High-pressure effects on the Diels–Alder reaction in room temperature ionic liquids

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ABSTRACT: The effect of pressure on the Diels–Alder reaction was examined in room temperature ionic liquids, followed by high-pressure FT-IR spectroscopy using pressures up to 150 MPa. Pressure enhances the kinetic sensitivity of the reaction. The kinetic effect of fluorophobic interactions was examined using ionic liquids with fluorous cations. Ionic liquids in combination with ZnI_2 as a Lewis acid catalyst were also studied under high pressure.

KEYWORDS: high pressure; ionic liquids; Diels–Alder reaction; fluorous effect; Lewis acid catalysts.

INTRODUCTION

Organic synthesis under high pressure is valid where the activation volume, $\Delta V^{\neq}$, is negative, providing its absolute magnitude sufficiently large ($\Delta V^{\neq} < -15\,\mathrm{cm^3\ mol^{-1}}$),[1] influencing a reaction by (i) accelerating the reaction, (ii) modifying regioselectivity and diastereoselectivity, and (iii) by causing changes to the chemical equilibrium.[2] The effect on chemical equilibrium and rates of reaction may be determined by the relationship between pressure and the Gibbs' enthalpy of reaction and activation, Eqn (1).

$$\Delta V = \left(\frac{\partial \Delta G}{\partial p}\right)_T = \left(-\frac{\partial \ln K_p}{\partial p}\right)_T \cdot RT$$
$$\Delta V^{\neq} = \left(\frac{\partial \Delta G^{\neq}}{\partial p}\right)_T = \left(-\frac{\partial \ln k_p}{\partial p}\right)_T \cdot RT \qquad (1)$$

where ΔV, $\Delta V^{\neq}$ are volumes of reaction and activation; K_p is equilibrium constant at pressure p; k_p is rate constant at p; ΔG, $\Delta G^{\neq}$ are Gibbs enthalpy and Gibbs enthalpy of activation.

The activation volume of a reaction is determined from the pressure dependence of the formation rate constant (k_f) and is a measure of the partial molar volume of the transition state with respect to the partial molar volumes of the reactants. The volume of reaction corresponds to the difference between the partial molar volumes of reactants and the products and is usually determined experimentally.[3]

High-pressure kinetics is a useful tool for the determination and the assessment of the mechanism of a reaction.[1] The volumes of activation deduced by such kinetic measurements are an indicator of the position of the transition state. However, $\Delta V^{\neq}$ does not result exclusively from volume modifications induced by the bond transformation, rather, it encompasses all the volume changes that occur during the progression of the reaction from the initial state, to the transition state, and within the transition state.[4] The activation volume $\Delta V^{\neq}$, Eqn (2), results from two main volume effects: first, intrinsic part ($\Delta V^{\neq}_{\mathrm{intr}}$) results from the formation or cleavage of bonds, and second, a solvation contribution ($\Delta V^{\neq}_{\mathrm{solv}}$) describing solvent effects on equilibria and rates under pressure.[5]

$$\Delta V^{\neq} = \Delta V^{\neq}_{\mathrm{intr}} + \Delta V^{\neq}_{\mathrm{solv}} \qquad (2)$$

The Diels–Alder reaction is one of the most important carbon-carbon bond forming reactions used to prepare cyclic structures, usually affording a mixture of isomers with the selectivity (and reaction rate) being solvent dependent. It is a prototypical high-pressure reaction, and has been extensively studied under pressure, because it shows a strong pressure-induced acceleration.[2,6] It is sometimes inhibited by the low reactivity of reagents, diene and dienophile, and/or instability of both reagents and cycloadducts under thermal or Lewis acid catalyzed conditions. Considerable improvements have often been made in these cases, but mostly under extreme conditions, *viz.* pressures up to 1500 MPa (sometimes in combination

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with high temperatures and/or the presence of catalysts).[2] The pressure effect on cycloaddition reactions has been widely explored in organic solvents,[1,7] aqueous solutions[8] and fluorous media,[9] and the influence of ionic liquids on the Diels–Alder reaction under high pressure has been mentioned in a review.[10]

Ionic liquids represent an interesting class of solvent in which to conduct Diels–Alder reactions, since they are polar and have no vapor pressure, potentially leading to high selectivities with the added advantage of facile product separation. A number of Diels–Alder reactions have been conducted in ionic liquids under ambient pressures[11–16] as well as reactions in the presence of Lewis acid catalysts.[13,14,17–19] From these studies it would appear that the selectivity of Diels–Alder reaction is dependent on the hydrogen bond donor capacity of the ionic liquids that can stabilize the transition state, with long substituents on the cation leading to lower selectivities and strong electrostatic associations between the ionic liquid ions resulting in a lower interaction between the ionic liquid and the transition state. In addition, π-orbital overlap promoted by a low energy LUMO and decrease in the presence of a low energy HOMO on the ionic liquid cation appear to promote the interaction between the transition state and the ionic liquid indicating that all type of interactions contribute towards the observed selectivity.

In this paper we investigate the influence of pressure on the Diels–Alder reaction in ionic liquids. An ionic liquid with a fluorous cation has been synthesized in order to study fluorophobic effects on the reaction, and the influence of the Lewis acid catalyst ZnI_2 in ionic liquids has also been studied under pressure.

RESULTS AND DISCUSSION

The Diels–Alder reaction of cyclopentadiene with two different dienophiles, methyl acralyte or acrolein (Scheme 1) in series of $[Tf_2N]^-$ based ionic liquids using pressures up to 150 MPa have been investigated.

Reactions were followed *in situ* by high-pressure IR spectroscopy and the reaction profiles were evaluated using Eqn (3) (further details are provided in supplementary information). Only an overall rate could be calculated from the spectroscopic data and therefore the selectivity was determined after reaction by ^{13}C NMR spectroscopy.

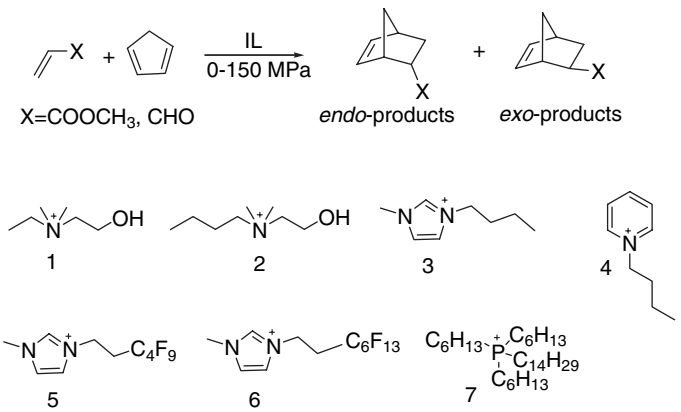
$$-\frac{d[A]}{dt} = [A]_t \cdot [B]_t \cdot k \qquad (3)$$

where $[A]_t$ is dienophile conectration; $[B]_t$ is cyclopentadiene concentration; k is rate constant.

Preliminary experiments were conducted using the cation *N*-ethyl-*N*-(2-hydroxyethyl)-*N*,*N*-dimethylammonium **1**, chosen because it had a prominent influence on the rate and the selectivity of the reaction at ambient pressure, due to the presence of a hydrogen bond donor moiety.[16] The reaction between cyclopentadiene and methyl acrylate was followed in **1**[Tf_2N] at different pressures and at different molar ratios of ionic liquid to substrate (Table 1).

Irrespective of the conditions used, *viz* temperature or concentration, the increase in the rate constant induced by pressure is similar. Since the reactions at 25 °C were relatively fast further reactions were monitored at 5 °C. The effect of pressure was studied at pressures between 0.1 and 150 MPa (Table 2). Pressure-induced acceleration of the reaction is greatest in **1**[Tf_2N] and least in **4**[Tf_2N]. The reaction rate and the pressure effect in dichloromethane are lower than that observed in the ionic liquids, whereas ethanol is superior to the ionic liquids in both these respects. Table 2 lists the rate constant ratios, calculated volumes of activation and θ values ($\theta = \Delta V_{25}^{\neq} : \Delta V_{25}$, where $\Delta V_{25} = -33.5$ for the reaction between cyclopentadiene and methylacrylate, and $\Delta V_{25} = -42.95$ for the reaction between cyclopentadiene and acrolein).[20]

Volumes of activation ($\Delta V^{\neq}$) were deducted from k values plotted against pressure (Fig. 1) and extrapolated using the El'yanov equation at 25 °C (Table 2, footnote c). ln k shows a linear dependence with pressure up to



Scheme 1. Diels–Alder cycloadditions studied and ionic liquid cation structures employed.

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Table 1. Rate constants for the reaction of cyclopentadiene with methyl acrylate in **1**[Tf_2N] ionic liquid at 0.1 and 100 MPa under various conditions (mol ratio of ionic liquid:methyl acrylate = 1:1 or 10:1)

	25 °C	Mol ratio 1:1	5 °C	Mol ratio 1:1	5 °C	Mol ratio 10:1
p [MPa]	$k^a \times 10^6$	σ	$k^a \times 10^6$	σ	$k^a \times 10^6$	σ
0.1	88.0	±0.5	21.9	±0.2	18.0	±0.3
100	238.1	±0.8	60.2	±0.6	46.2	±0.4

[a] In [$M^{-1}\,sec^{-1}$], standard deviation at the 95% confident level.

Table 2. Effect of pressure on rate constants for the reaction between cyclopentadiene and methyl acrylate or acrolein at 5 °C, rate constant ratios, volumes of activation, and θ values

		0.1 [MPa]		50 [MPa]		100 [MPa]		150 [MPa]					
Solvent	Substrate	$k^a \times 10^6$	σ	$k^a \times 10^6$	σ	$k^a \times 10^6$	σ	$k^a \times 10$	σ	$k_{100}/k_{0.1}$	$\Delta V_5^{\neq b}$	$\Delta V_{25}^{\neq c}$	θ
1[Tf_2N]	Methyl acrylate	21.9	±0.2	39.1	±0.2	60.2	±0.6	88.3	±0.3	2.7	−23.4	−25.7	0.8
2[Tf_2N]	Methyl acrylate	19.6	±0.1	31.0	±0.5	50.5	±0.3	71.0	±0.5	2.6	−22.5	−24.7	0.7
3[Tf_2N]	Methyl acrylate	16.9	±0.2	27.3	±0.3	41.3	±0.2	57.2	±0.4	2.4	−20.6	−22.6	0.7
4[Tf_2N]	Methyl acrylate	15.2	±0.6	19.0	±0.4	28.1	±0.7	44.0	±0.4	1.9	−15.3	−16.8	0.5
CH_2Cl_2	Methyl acrylate	9.3	±0.7			18.2	±0.5			2.0	−14.6	−16.1	0.5
EtOH	Methyl acrylate	22.6	±0.6			88.7	±0.8			4.0	−31.7	−34.7	1.0
1[Tf_2N]	Acrolein	209	±1	432	±2	604	±2	1190	±14	2.9	−24.6	−27.0	0.6
2[Tf_2N]	Acrolein	182	±1	393	±4	501	±3	1111	±12	2.8	−23.4	−25.7	0.6
3[Tf_2N]	Acrolein	73	±1	136	±3	194	±3	354	±4	2.7	−22.6	−24.8	0.6
4[Tf_2N]	Acrolein	71	±1	111	±2	185	±4	326	±5	2.6	−22.2	−24.3	0.6
CH_2Cl_2	Acrolein	47	±1			131	±2			2.6	−23.4	−25.6	0.6
EtOH	Acrolein	136	±1			683	±3			5.0	−37.4	−41.0	1.0
5[Tf_2N]	Methyl acrylate	23.3	±0.6			47.2	±0.4			2.0	−16.4	−18.0	
6[Tf_2N]	Methyl acrylate	12.3	±0.1			24.7	±0.4			1.9	−15.4	−16.1	
7[$PF_3(C_2F_5)_3$]	Methyl acrylate	19.2	±0.3			29.2	±0.6			1.5	−9.7	−10.7	

[a] In [$M^{-1}\,sec^{-1}$] and the standard deviation is at the 95% confident level.
[b] In [$cm^3\,mol^{-1}$] determined from the pressure dependence of the rate constant at 5 °C, precision of $\Delta V^{\neq}$ values is estimated to be ±0.5 $cm^3\,mol^{-1}$.
[c] Determined from the extrapolated dependence from $\Delta V_T^{\neq}$ using the El'yanov equation $\Delta V_{25}^{\neq} = \Delta V_T^{\neq}/[1 + 4.43 \times 10^{-3}\,K^{-1}$ (T-25 °C)].[27,28]

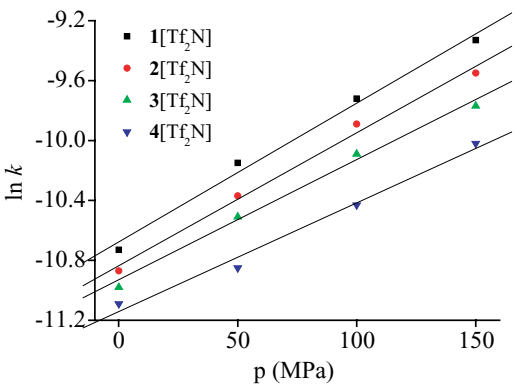

Figure 1. Plotted ln k values against pressure for the reaction between cyclopentadiene and methyl acrylate in different ionic liquids (goodness of fit, $R > 0.99$ was observed in all cases)

150 MPa allowing the activation volumes to be estimated. Calculated θ values for the ionic liquids are lower than unity, indicating the transition state is not rigid and is poorly ordered,[4] which most likely is attributable to a weakening of the concertedness of the reaction, possibly due to steric hindrance from the ionic liquid components. Although these data suggest that the transition state is not well defined, there is some ordering, as indicated by the difference in the calculated activation volumes, between **1**[Tf_2N] and **4**[Tf_2N], $\Delta\Delta V^{\neq} = 9 \pm 0.5\,cm^3\,mol^{-1}$ for the reaction of cyclopentadiene and methyl acrylate, and $\Delta\Delta V^{\neq} = 3 \pm 0.5\,cm^3\,mol^{-1}$ for the reaction between cyclopentadiene and acrolein (lower because the reaction rates are higher with acrolein).[21] Overall, the high-pressure trends follow those observed at ambient pressure.

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Table 3. Effect of pressure on the *endo:exo* selectivity of the reaction between cyclopentadiene and methyl acrylate or acrolein at 5 °C in different ionic liquids

p [MPa]	Substrate	**1**[Tf_2N]	**2**[Tf_2N]	**3**[Tf_2N]	**4**[Tf_2N]	**5**[Tf_2N]	**6**[Tf_2N]	**7**[$PF_3(C_2F_5)_3$]
0.1	Methyl acrylate	5.6	5.2	4.3	4.2	4.6 (4.1)[a]	4.5 (3.9)[a]	3.5
50	Methyl acrylate	5.8	5.4	4.5	4.3			
100	Methyl acrylate	6.0	5.5	4.6	4.5	5.2	5.0	4.0
150	Methyl acrylate	6.2	5.7	4.8	4.7			
0.1	Acrolein	6.0	5.6	4.6	4.4			
50	Acrolein	6.2	5.8	4.7	4.5			
100	Acrolein	6.4	5.9	4.9	4.7			
150	Acrolein	6.6	6.1	5.1	4.8			

Yields in all the reactions exceed 95%.
[a] Selectivity obtained when an alkyl chain the same length as the fluorous chain was used.[16]

Pressure influences selectivity due to secondary orbital interactions which induce a larger contraction of the volume of the *endo* transition state.[22,23] The change in *endo:exo* selectivity with pressure reveals only a modest improvement (Table 3).

Highly fluorinated (fluorous) solvents give rise to large negative volumes of activation for the Diels–Alder reaction.[24] Although fluorophobic interactions decrease with increasing pressure, many reactions are activated by pressure in fluorophobic media.[9] Thus, the effect of pressure on the Diels–Alder reaction conducted in the fluorous ionic liquids **5**[Tf_2N] and **6**[Tf_2N] (Scheme 1), prepared according to a modified literature protocol,[25] was investigated. An ionic liquid with a large perfluorinated anion was also studied since it has been shown to be somewhat fluorous-like in nature.[26] In **5**[Tf_2N] the rate constant at ambient pressure is higher than in the other ionic liquids, approximately equivalent to ethanol. In **6**[Tf_2N] and **7**[$PF_3(C_2F_5)_3$] the rate constants are similar to the other ionic liquids. In contrast to fluorous molecular solvents activation volumes are less negative (Table 2) and changes in *endo:exo* selectivity remain small (Table 3).

Pressure effects on the Diels–Alder reaction between cyclopentadiene and methyl acrylate in **3**[Tf_2N] in the presence of the Lewis acid catalyst ZnI_2 (0.2 mol%) was investigated (Table 4). The experimentally determined activation volume in the presence of ZnI_2 [$\Delta V_{25}^{\neq} = -27.1\,cm^3\,mol^{-1}$] is $4.5\,cm^3\,mol^{-1}$ more negative than with no catalyst, and the calculated θ value [0.81] is closer to unity, indicating a progression of the transition state along the reaction coordinates. Indeed, both the reaction rate and selectivity of the reaction increase slightly in the presence of ZnI_2.

CONCLUSIONS

From this study we are able to show how at the high pressure ionic liquids follow those trends observed at ambient pressure. Higher reaction rates and selectivities are obtained in the *N*-alkyl-*N*-(2-hydroxyethyl)-*N*, *N*-dimethylammonium liquids where hydrogen bond donor moieties are separated somewhat from the center of charge on the cation, although as the length of an alkyl chain on the ionic liquid cation increases the reaction rates and selectivities decrease, presumably due to steric interactions between the transition state and the cation. Ionic liquids are superior solvents to polar ones such as dichloromethane, but less effective than polar protic alcohols, the activation volume in all the ionic liquids studied was less negative than that of ethanol. Modest improvements in selectivities and rate constants are observed in the presence of fluorous groups, either on the cation or on the anion.

Table 4. Effect of pressure on rate constants and selectivities for the reaction of cyclopentadiene and methyl acrylate in **3**[Tf_2N] containing ZnI_2

	3[Tf_2N] (0.2 mol% ZnI_2)			**3**[Tf_2N]		
p [MPa]	$k^a \times 10^6$	σ	*endo:exo* ratio	$k^a \times 10^6$	σ	*endo:exo* ratio
0.1	23.1	±0.3	5.4	16.9	±0.2	4.3
50	45.0	±0.5	5.6	27.3	±0.3	4.5
100	67.3	±0.4	5.8	41.3	±0.2	4.6
150	101.0	±0.7	6.0	57.2	±0.4	4.8

[a] In [$M^{-1}\,sec^{-1}$], the standard deviation is at the 95% confident level.

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For all the ionic liquids studied θ values were below one, which indicates that the transition state is poorly ordered, thus implying that design of ionic liquids with cations that contain specific groups to facilitate alignment of the substrate to improve selectivities may not lead to vastly improved systems. A far simpler and more effective approach involves the incorporation of Lewis acid anions as a component with the ionic liquid, which can lead to vastly improved selectivities, as reported previously for chloroaluminate ionic liquids.[13]

EXPERIMENTAL SECTION

Methyl acrylate was distilled prior to use and cyclopentadiene was obtained by cracking dicyclopentadiene, distilled under reduced pressure, and stored at $-70\,^{\circ}C$. The ionic liquids illustrated in Scheme 1, that is, **1**[Tf_2N], [16]**2**[Tf_2N],[16]**3**[Tf_2N],[29]**4**[Tf_2N],[30]**6**[I],[25]**6**[Tf_2N],[31]**5**[I],[32] and **5**[Tf_2N][32] were prepared according to literature procedures. Trihexyltetradecylphosphonium hexafluorophosphate **7**[$PF_3(C_2F_5)_3$] was purchased from Fluka.

Diels–Alder reactions

Typically, cyclopentadiene (0.4 mL, 5.0 mmol) and methyl acrylate (0.3 mL, 3.3 mmol) were added to ionic liquid or organic solvent (0.8 mL). For catalyzed reactions the ionic liquid was doped with ZnI_2 (0.2 mol%) and stirred overnight before use. Alternatively, cyclopentadiene (0.4 mL, 5.0 mmol) and acrolein (0.2 mL, 3.3 mmol) were added to ionic liquid or organic solvent (0.8 mL). In the reactions using fluorous ionic liquids, cyclopentadiene (0.12 mL, 1.5 mmol) and methyl acrylate (0.09 mL, 1.0 mmol) were added to ionic liquid (0.4 mL). The reactions were carried out in a high-pressure IR cell with sapphire windows at 25 or 5 °C for 24 h and spectra were recorded every 3 or 10 min.[33] The cell was thermostated and ethanol was used as the pressurizing liquid. FT-IR spectroscopic data were analyzed using TimeBase version 2.0 (Perkin Elmer). Numerical analyses were carried out with Scientist 2.0 (Micromath). After reaction, the products were analyzed by ^{13}C NMR spectroscopy and GC. NMR spectra were measured on Bruker DRX 400 MHz spectrometer. NMR data were analyzed using WinNMR 6.1 (Bruker). GC analyses were carried out on a Varian Chrompack CP-3380 equipped with capillary (25 m × 0.25 mm, using He as carrier gas).

Methyl 5-norbornene-2-carboxylate *endo* product

^{13}C NMR (neat, 400 MHz) 172.2 (s), 134.0 (d, $J = 169$ Hz), 128.7 (d, $J = 169$ Hz), 53.4 (t, $J = 143$), 49.0 (q, $J = 147$ Hz), 42.2 (d, $J = 149$ Hz), 39.0 (d, $J = 132$ Hz), 38.8 (d, $J = 154$ Hz), 26.3 (t, $J = 132$ Hz) ppm.

Methyl 5-norbornene-2-carboxylate *exo* product

^{13}C NMR (neat, 400 MHz) 173.7 (s), 134.4 (d, $J =$ 170 Hz), 129.4 (d, $J = 170$ Hz), 53.5 (t, $J = 144$) 49.3 (q, $J = 147$ Hz), 43.0 (d, $J = 148$ Hz), 39.1 (d, $J = 132$ Hz), 39.0 (d, $J = 154$ Hz), 21.6 (t, $J = 131$ Hz) ppm.

SUPPORTING INFORMATION

Kinetic data are available as supporting information.

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