RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2015, **5**, 2994

Kinetic and mechanistic investigations of the Baylis–Hillman reaction in ionic liquids†

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We report here a quantitative study of the kinetics and mechanism of the Baylis–Hillman reaction in the presence of ionic liquids as solvent media. Apparently, a simple Baylis–Hillman reaction can occur by two different exclusive mechanisms in ionic liquids. The delicate balance of these mechanisms is maintained by the ionic environment employed. The main features of the possible mechanism have been described here along with interesting kinetic consequences. The measurement of rate constants and activation energy parameters demonstrate that as the medium becomes basic, the order of the reaction changes from 1 to 2. An unexpected change in the mechanism of the reaction is observed with a change in the nature of the ionic liquid. The Linear Solvation Energy Relationship has also been used as an investigating tool to delineate the respective contributions of the cation and anion of the ionic liquid. The observation strongly dictates the dependency of the mechanism of the Baylis–Hillman reaction on the nature of the anion of the ionic liquids undertaken for this study.

Received 30th September 2014
Accepted 28th November 2014

DOI: 10.1039/c4ra14764b

www.rsc.org/advances

Introduction

The Baylis–Hillman reaction offers a potential strategy to construct highly functionalized products with a new stereocentre.[1] The Baylis–Hillman reaction is essentially a three-component reaction involving coupling of the α-position of the activated alkene with carbon electrophiles under the catalytic influence of a tertiary amine, providing a simple and convenient methodology for synthesis of densely functionalised molecules. In fact, the ease of selectivity simplifies the process of assembling a carbon framework, which involves creativity and is thus categorized as an important research topic in science.[2–10] Several articles have appeared in the literature elaborating the basic mechanistic aspects and applications of the synthesized products.[11–13] More recently, ionic liquids have been employed as solvent media for catalyzing many important organic reactions.[14–17] Ionic liquids possess many interesting properties such as wide temperature window, very low vapour pressure, recyclability *etc.* which make them different from other conventional solvents and facilitate attributes which are of fundamental interests to chemists. An ionic liquid is made up of cation and anion, either of which or both may interact with the reactants and affect the course of the reaction. Baylis–Hillman reaction has also been carried out in ionic liquids.[18] There are reports describing acceleration of DABCO-catalysed Baylis–Hillman reaction in the imidazolium based ionic liquid.[19] However, it was later shown that the imidazolium salts, with hydrogen at C-2 position, are deprotonated under mildly basic conditions, forming corresponding carbenes with undesirable side reactions.[20] This undesired deprotonation was partly overcome by the application of C-2 substituted imidazolium salts for carrying out Baylis–Hillman reaction.[21] Efficient catalysis with good yield and reduced reaction times were reported for pyridinium based ionic liquids too.[22] However, the need of application of efficient ionic liquids for carrying out Baylis–Hillman reaction still stimulates a continuous research effort. In spite of several attempts made in the past, the mechanism of Baylis–Hillman reaction is still an issue of debate. In 1986, Hill and Isaacs have proposed a mechanism based on pressure dependence, rate and kinetic isotope effect.[23] They proposed that α-proton cleavage was not taking place in the rate determining step of the reaction. A kinetic study of the reaction between acetaldehyde and acrylonitrile was followed and the rates observed depended linearly on the first power of each concentration, confirming the empirical rate expression as:

$$\text{rate} = k_3[\text{MeCHO}][\text{ACN}][\text{DABCO}]$$

Based upon these studies they proposed the mechanism of the Baylis–Hillman reaction to be proceeding in three important steps as (a) Michael addition, involving attack of a base on an activated alkene, forming an enolate (b) nucleophilic attack of the enolate on an aldehyde and (c) proton transfer and the

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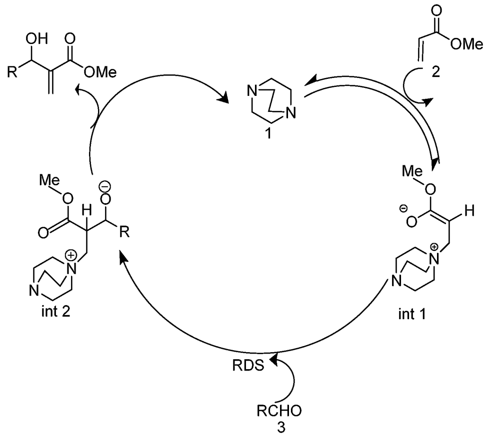
† Electronic supplementary information (ESI) available: This section includes procedure for synthesis of ionic liquids, GC parameters, general procedure of reaction, GC chromatogram, NMRs of product and ionic liquids. See DOI: 10.1039/c4ra14764b

elimination of base resulting into product formation (Scheme 1).

Later, Bode and Kaye, using acrylates also supported Hill and Isaacs mechanism.[24] A significant contribution was made by McQuade and co-workers who discovered a new pathway of the reaction.[25] Surprisingly, they observed that when the reaction was carried out in polar aprotic solvent as DMSO, a new mechanism was operating based on hemiacetal intermediate. The reaction showed second order dependence on aldehyde concentration. Although the report was quite intriguing, the mechanistic investigation of the reaction in a varied range of solvents is still less studied. This report encouraged us to determine the kinetic aspects of this reaction in a variety of ionic liquids.[26] In this report from our lab we reported that the rate determining step is second order in aldehyde, while first order in acrylate and DABCO when carried out in ethylsulfate based ionic liquids. These results were in contrast to the observation made in organic solvents. From the earlier studies the role of cations of ionic liquids in catalysing the reaction is still in the state of infancy. In order to investigate the role of cations and anions, Linear Solvation Energy Relationship (LSER) has been employed here as a part of our investigating tool. To the best of our knowledge the influence of various ionic liquids on the reactivity of Baylis–Hillman reaction by LSER has not been systematically reported earlier. As a part of our investigation of various organic reactions in environment benign media.[27–29] we herein investigate Baylis–Hillman reaction in a variety of solvents with differing cations and anions. The roles of anions and cations have been further delineated by LSER.

Experimental section

1,4-Diazabicyclo [2.2.2]octane [DABCO] with (>99% purity) and *p*-nitrobenzaldehyde, (>98% purity) were obtained from M/S Sigma-Aldrich company and were used without further purification. Methanol, dichloromethane, toluene, dimethylsulfate, ethyl acetate were used as obtained from Merck Germany. Methyl acrylate was distilled prior to use. 1-Morpholine, 1-bromobutane, pyrrolidine, piperidine, 1-methylimidazole, pyridine, Lithium bis(trifluoromethane)sulfonimide >99% purity was used as obtained from M/S Sigma-Aldrich company.



Scheme 1 Mechanism of Baylis–Hillman reaction as proposed by Hill and Isaacs.

Synthesis of the ionic liquids

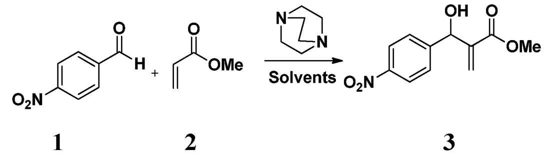
All ionic liquids were synthesized as per the procedure given in literature. Detailed synthesis of the ionic liquids is given in the ESI.† The water content of all ionic liquids was measured by Karl-Fischer coulometer and was found to be less than 50 ppm.

Kinetic measurements

The reaction was initiated by the addition of methyl acrylate 0.9028 ml (1 M) to the stirred solution of *p*-nitrobenzaldehyde and 1 ml of DABCO (1 M) in a given solvent. The temperature was maintained by Julabo constant temperature bath maintained at 25 °C with an accuracy of ±0.01 K. The progress of the reaction was monitored by withdrawing 1 ml of reaction mixture in ether at appropriate time intervals. Chlorobenzene was used as an internal standard. The extracted sample was injected for GC analysis using a Varian CP-3800 gas chromatogram. All reactions were monitored before 15% conversion. The k_2 values were obtained from the integration of the peak area of the product with respect to internal standard at different intervals of time. Slope of $x/a(a-x)$ *versus* time plot and of $\ln(a/a-x)$ *versus* time plot gave the value of pseudo second order and of first order rate constant respectively. Relative peak area was at prior calibrated with respect to the pure product of Baylis–Hillman reaction. No byproducts were observed during entire reaction. Order plots were made by plotting rate *versus* concentration of *p*-nitrobenzaldehyde. Linear dependence of the rate of reaction on *p*-nitrobenzaldehyde concentration exhibited reaction to be of first order and nonlinear dependence was an indication of second order. The rate constants measured were reproducible to ±3%.

Determination of activation parameters

Temperature dependent rate constants k_2 was determined in different ionic liquids at 5 different temperatures. Required temperature was maintained by Julabo constant temperature bath with an accuracy of ±0.01 K. The reaction was started by the addition of methyl acrylate, 0.9028 ml (1 M) to a stirred solution of *p*-nitrobenzaldehyde (0.04 M) and DABCO (1 M) in 1 ml of solvent. The progress of the reaction was followed by GC. 1 ml of aliquot was withdrawn from the reaction mixture at appropriate time interval and was further diluted and extracted in ether. The extracted sample was then injected for GC



Scheme 2 The investigated Baylis–Hillman reaction.

analysis. Chlorobenzene was used as an internal standard. Calculation of k_2 has already been explained in the kinetic measurement section. Arrhenius and Eyring equation were used for the calculation of activation parameters. Each experiment was carried out in triplicate and the standard error in measurement was ±6% [Pyr][HSO_4], ±8% [Opy][HSO_4] and 10% for [Opyr][HSO_4].

Results and discussion

As shown in Scheme 2, we have investigated the reaction between *p*-nitrobenzaldehyde, **1** methyl acrylate, **2** and DABCO as a catalyst in the presence of different ionic liquids used as solvents. Investigation of the reaction in other electron rich aldehydes such as benzaldehyde and anisaldehyde was thwarted since the reaction was sluggish and took considerable longer reaction time for its completion.[7a] The nature of the solvent is an important determinant of the solute–solvent interactions and resultant kinetic parameters. As ionic liquids have the potential to act as solvent media, different from that offered by any other solvent, it is expected that ionic liquids may influence the kinetics of the Baylis–Hillman reaction. In order to discern the role of cations of ionic liquids on Baylis–Hillman reaction, we present in the current investigation the mechanistic aspects in the presence of ionic liquids. The ionic liquids synthesized and used in the reaction were [Opy][HSO_4], [Opyr][HSO_4], [Opip][HSO_4], [MeMo][$MeSO_4$], [Pyr][HSO_4], [Pyr][CH_3COO], [Pyr][HCOO], [Mbpyr][NTf_2], [Pyr][NO_3], [Bmim][Br], [Pyr][CF_3COO] and [Opipe][HSO_4]. Amino acids and imidazolium based ionic liquids cannot be used due to the involvement of side reactions.[20]

The kinetic results in these ionic liquids together with their acronyms and names are given in Table 1. The plot of $(\partial c/\partial t)$ *versus* concentration for [Pyr][NO_3], [Pyr][CH_3COO], [Pyr][HCOO], [Mbpyr][NTf_2], [Pyr][CF_3COO] showed linear dependence of rate of the reaction on *p*-nitrobenzaldehyde concentration. Interestingly, an order of one indicated the involvement of one equivalent of *p*-nitrobenzaldehyde in the rate determining step of reaction. Rate plots are given in Fig. 1 for illustration. However, interestingly when the reaction was carried out in [Opyr][HSO_4] and [Opy][HSO_4], the reaction the reaction showed an order of 2. In order to ascertain the role of sulfate based ionic liquids, reaction was also carried out in [Py][HSO_4], [Opip][HSO_4] and [MeMo][$MeSO_4$]. The plot of $(\partial c/\partial t)$ *versus* concentration for these ionic liquids also exhibited second order dependence on *p*-nitrobenzaldehyde concentration. The rate plots are given in Fig. 2. An order of two suggested involvement of two equivalents of aldehyde in the rate determining step of the reaction. This observation suggested that probably there was a change in the mechanism of the reaction with the change in the structure of ionic liquid. The yield obtained in case of [Pyr][HSO_4] (with an order of 2) and [Pyr][HCOO] (with an order of 1) ionic liquids were 70% and 68%, respectively. The possibility of acid–base equilibria between DABCO and the ionic liquid cationic component was thwarted since the moieties chosen as cationic component was sufficiently basic as compared to that of DABCO. This eliminated the possibility of the proton exchange between the catalyst taken and the ionic liquids. Henceforth, any possibility of side reaction can be neglected in the present study.[30] Further, to investigate the role of cations in the kinetic and mechanistic aspect of reaction, a number of ionic liquids with same anion and different cations were synthesized. No change was however observed in the order of the reaction upon changing the cation of ionic liquids. This was quiet intriguing as it indicated the nominal role played by the cations of ionic liquids in influencing the mechanism of the reaction. [Opyr][HSO_4] ionic liquid was solid at room temperature and the kinetic study was performed at higher temperatures (55 °C). Higher rate constants observed in [Opyr][HSO_4] can be explained by the influence of higher temperature employed for carrying out the experiments. [Pyr][HSO_4], [MeMo][$MeSO_4$] and [Opip][HSO_4] showed higher k_2 values due to high value of solvatochromic parameter, β, 0.966. β parameter is a measure of the basicity or electron accepting tendency of the anions of ionic liquids. Higher value of β indicates presence of higher electron density on the anions of ionic liquids, which can probably greatly affect the kinetics of the reaction by interacting strongly with the zwitterionic species formed during the course of the reaction. Other anions based on $HCOO^-$, NTf_2^-, CF_3COO^-, CH_3COO^-,

Table 1 Kinetic data for the reaction of *p*-nitrobenzaldehyde **1** and methyl acrylate **2** with DABCO in different ionic liquids

Acronyms	Names of ionic liquids	Aldehyde order, *n*	k_2 (pseudo rate constant)
[Opyr][HSO_4]	1-Octylpyrrolidinium hydrogensulfate	2	1.18×10^{-3} M^{-1} s^{-1}
[Opy][HSO_4]	1-Octylpyridinium hydrogensulfate	2	7.35×10^{-4} M^{-1} s^{-1}
[Opip][HSO_4]	1-Octylpiperidinium hydrogensulfate	2	1.22×10^{-3} M^{-1} s^{-1}
[Pyr][HSO_4]	Pyrrolidinium hydrogensulfate	2	1.35×10^{-3} M^{-1} s^{-1}
[MeMo][$MeSO_4$]	1-Methylmorpholinium methylsulfate	2	1.13×10^{-3} M^{-1} s^{-1}
[Pyr][NO_3]	Pyrrolidinium nitrate	1	3.46×10^{-5} s^{-1}
[Pyr][CH_3COO]	Pyrrolidinium acetate	1	3.33×10^{-5} s^{-1}
[Pyr][HCOO]	Pyrrolidinium formate	1	4.15×10^{-5} s^{-1}
[MbPyr][NTf_2]	1-Butyl-3-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	1	4.00×10^{-5} s^{-1}
[Pyr][CF_3COO]	Pyrrolidinium trifluoroacetate	1	1.94×10^{-5} s^{-1}
[Bmim][Br]	1-Butyl-3-methylimidazolium bromide	Too fast	—
[Opipe][HSO_4]	1-Octylpiperazinium hydrogensulfate	Solid < 90 °C	—

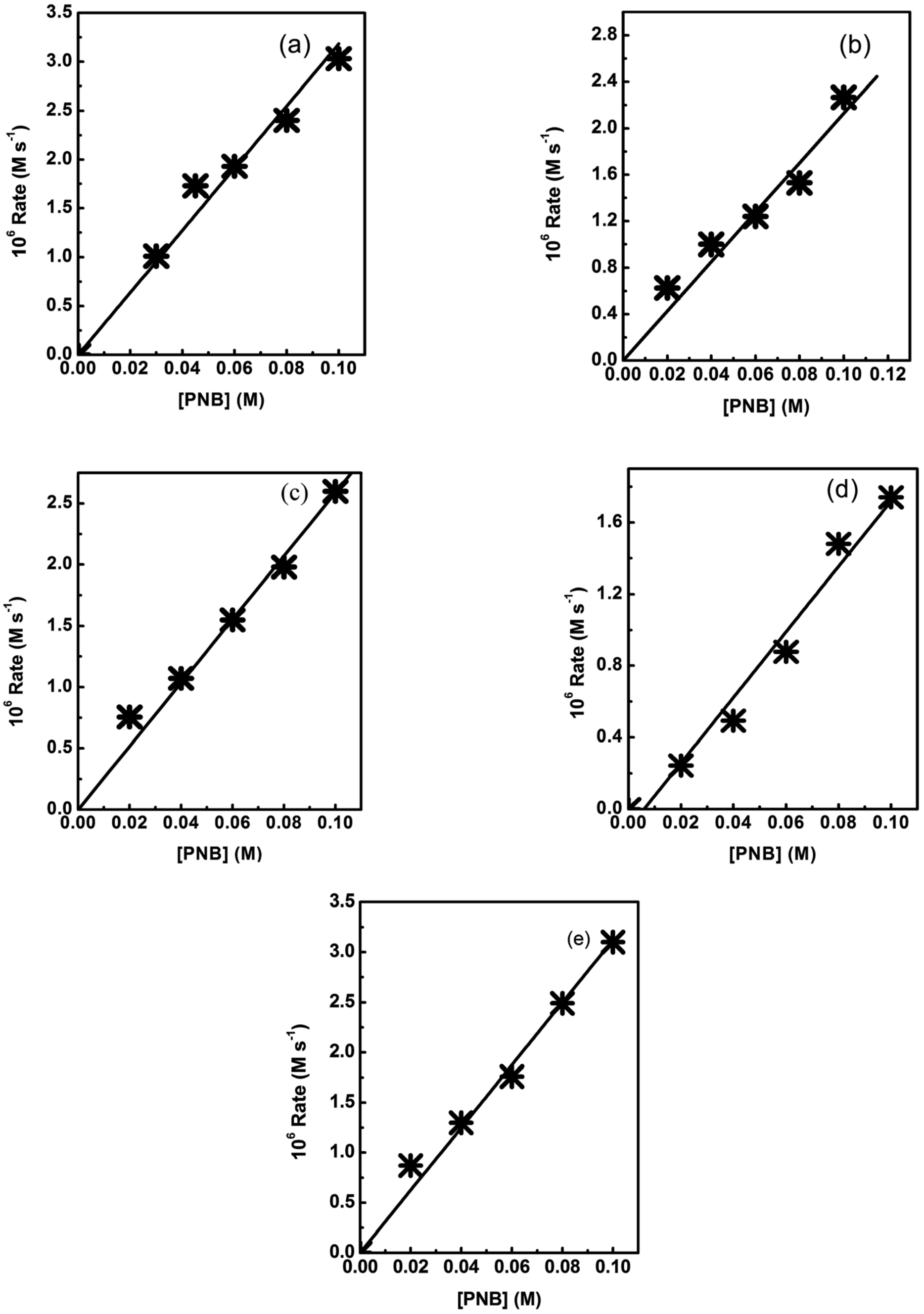


Fig. 1 The plots of the rate, $(\partial c/\partial t)$ *versus* concentration of **1** for the reaction of **1** with **2** in presence of DABCO in (a) [Mbpyr][NTf$_2$], correlation coefficient, $r = 0.0.982$, (b) [Pyr][CH$_3$COO], $r = 0.958$, (c) [Pyr][NO$_3$], $r = 0.994$, (d) [Pyr][CF$_3$COO], $r = 0.980$, (e) [Pyr][HCOO], $r = 0.987$.

NO_3^- had comparatively lower rate constants of the reaction due to the lower β values.[31]

Eyring activation parameters

In order to obtain greater insight into the mechanism of the reaction activation parameters, $\Delta^{\neq}H$ and $\Delta^{\neq}S$ were both determined using Eyring equation. $E_a^{\neq}$ was calculated from Arrhenius equation. The reaction in [Pyr][HSO$_4$] and [Opy][HSO$_4$] was carried out at 25, 35, 45, 55 and 65 °C. However for [Opyr][HSO$_4$] the reaction was carried out at 50 to 70 °C at an interval of 5 °C. The plots of $\ln(k/T)$ *versus* $1/T$ are given in Fig. 3 and of $\ln k$ *versus* $1/T$ are given in Fig. 4. $\Delta^{\neq}H$, $\Delta^{\neq}S$ and $E_a^{\neq}$ values were calculated from the slope and intercept of the graphs. The values are reported in Table 2. The observed magnitude of entropy for the reaction undertaken can credibly be associated with a process in which two successive bond formations occurred in conjunction with development of full charges. $E_a^{\neq}$ for [Pyr][HSO$_4$] is minimum which is in accordance of observation of higher rate constants of the reaction. $E_a^{\neq}$ 'observed for [Opy][HSO$_4$] was comparatively higher. This

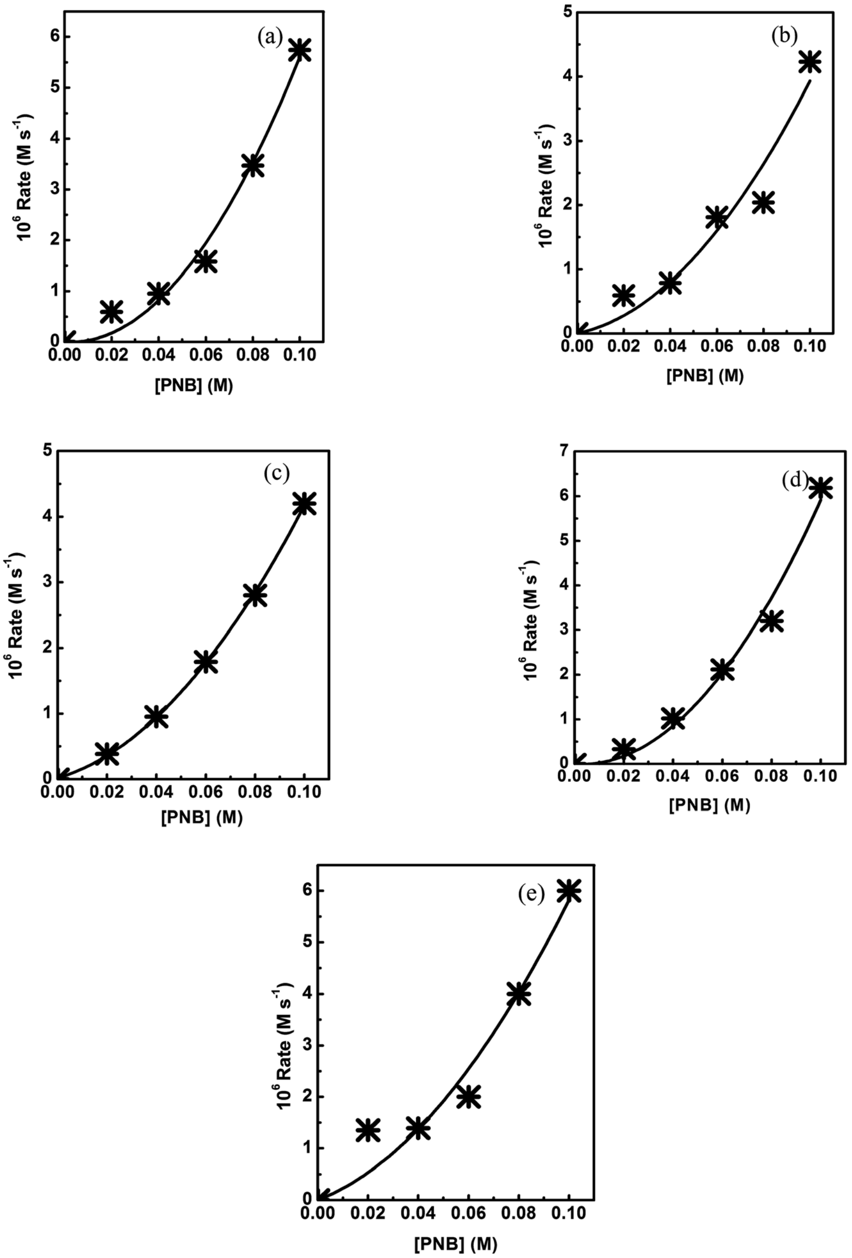


Fig. 2 The plots of the rate, ($\partial c/\partial t$) *versus* concentration of **1** for the reaction of **1** with **2** in presence of DABCO in (a) [Opip][HSO_4], correlation coefficient, $r = 0.997$, (b) [Opy][HSO_4], $r = 0.952$, (c) [MeMo][$MeSO_4$], $r = 0.999$, (d) [Pyr][HSO_4], $r = 0.985$ (e) [Opyr][HSO_4], $r = 0.961$.

can be a determinant factor in the observed slow pace of the reaction as reported in Table 1. Higher enthalpy of activation observed for [Opyr][HSO_4] can be explained by a noticeable change of the reaction from being exergonic to endergonic. This can provide a rationalization of the fact that the reaction cannot be performed at elevated temperatures. Higher entropy for reaction in [Opyr][HSO_4] suggests that bond formation becomes comparatively difficult at elevated temperatures.[32] Inspite of unfavourable $\Delta^{\neq}S$ the reaction carried out in [Opyr][HSO_4] possess k_2 of the order of 1.18×10^{-3} M^{-1} s^{-1}. This can be explained by very high β value of the sulfate based ionic liquids. Interestingly, presence of sulfate based anions makes thermodynamically unfavorable reaction, kinetically favorable. In order to elucidate the effect of longer alkyl chain length on the kinetics and mechanism of the reaction, [Opyr][HSO_4] and [Opy][HSO_4] ionic liquids were also deeply scrutinized. Results indicate that there is an increase in the $E_a^{\neq}$ energy upon moving from [Pyr][HSO_4] to [Opyr][HSO_4] suggesting that increase in the alkyl chain length of the cation can have detrimental effect on the rate of the reaction. Irrespective of increased activation energy barrier, the observed order of the reaction in [Pyr][HSO_4], [Opyr][HSO_4] and [Opy][HSO_4] remains 2. This is a very important finding that the mechanism of the reaction is independent of the alkyl chain length of the cation. The reaction follows the same pathway in the investigated ionic liquids. Long alkyl chain length of the cation is acting as a determinant to slow down the

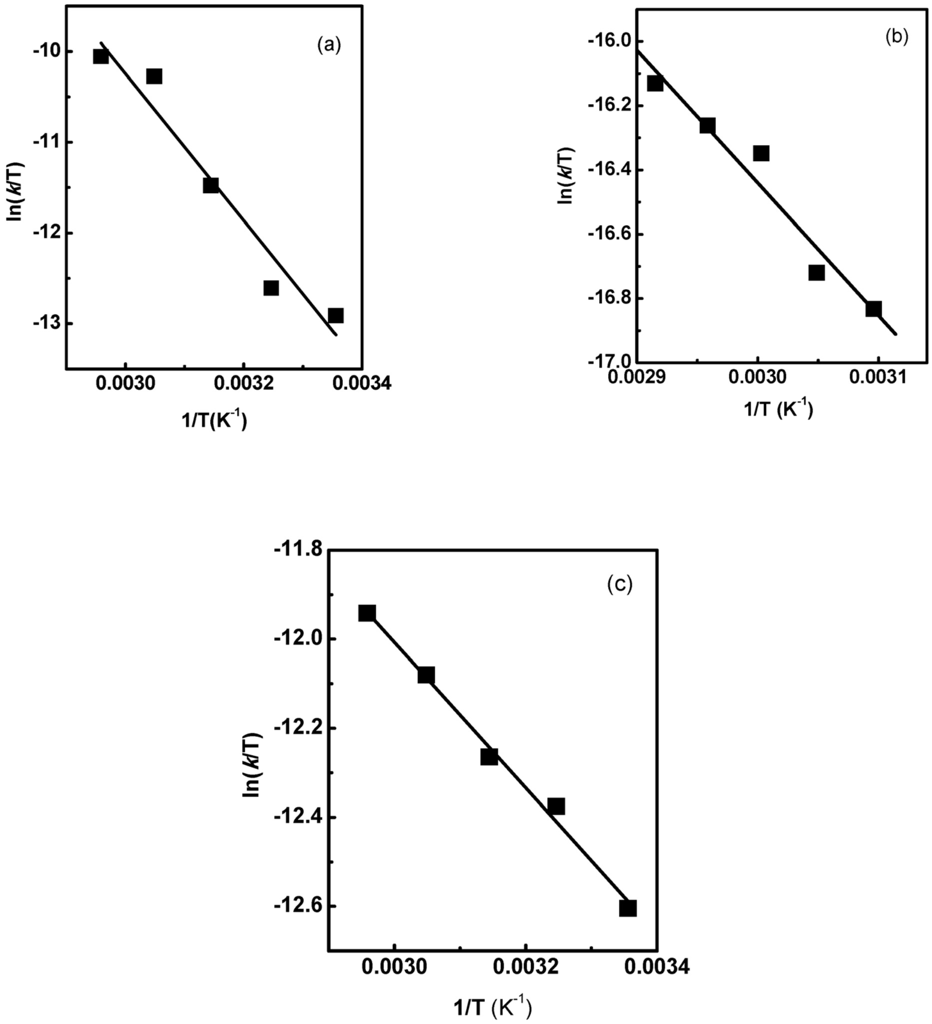


Fig. 3 Eyring plots (ln(*k*/*T*) *vs.* 1/*T*) for the reaction of *p*-nitrobenzaldehyde, **1** and methyl acrylate, **2** with DABCO in (a) [OPy][HSO_4] (b) [OPyr][HSO_4] (c) [Pyr][HSO_4].

reaction velocity as shown in Table 1. The interaction of the cation of ionic liquid with the reactants is comparatively weaker as compared to that of the anions. This may be due to the higher charge density on the sulfate based anions as compared to that of the cations. Electron rich anion can influence the reaction mechanism, containing charged species, in a more rational way as compared to that of cation.

Solvent-reactivity relationship

One of the most comprehensive and widely used solvent scales for understanding and interpreting solvent behaviour in reaction dynamics is linear solvation energy relationship (LSER). The use of solvatochromic probes for the characterization of molecular environment of reactants by LSER is well documented in the literature. The interaction of solvatochromic dyes with pure solvents or mixtures are a combination of many effects. The basic premise of linear solvation energy relationship is that attractive solute–solvent interaction can be represented as a linear combination of nonspecific dipolarity/polarizability (π^*) and specific hydrogen bond formation effect. Latter is further divisible into hydrogen bond accepting tendency (β) and hydrogen bond donar tendency (α). A variety of interactions varying from intermolecular specific and non specific solute–solvent interactions can be described by a concept of LSER given by:

$$(\mathrm{XYZ}) = (\mathrm{XYZ})_0 + a\mathrm{A} + b\mathrm{B} + c\mathrm{C}$$

where $(\mathrm{XYZ})_0$ represents property in a nonpolar medium, *a*, *b*, and *c* are coefficients which shows the dependence of physical and chemical properties (XYZ) in a particular solvent on various parameters of the solvent. The origin of the equation is from Kamlet–Taft equation which has been verified many times in the literature. It is one of the most successful quantitative methods for describing solvent effect with a multiparameter equation. The most established multivariate of LSER is that of Kamlet and Taft given by:[33]

$$(\mathrm{XYZ}) = (\mathrm{XYZ})_0 + a\alpha + b\beta + c\pi^*$$

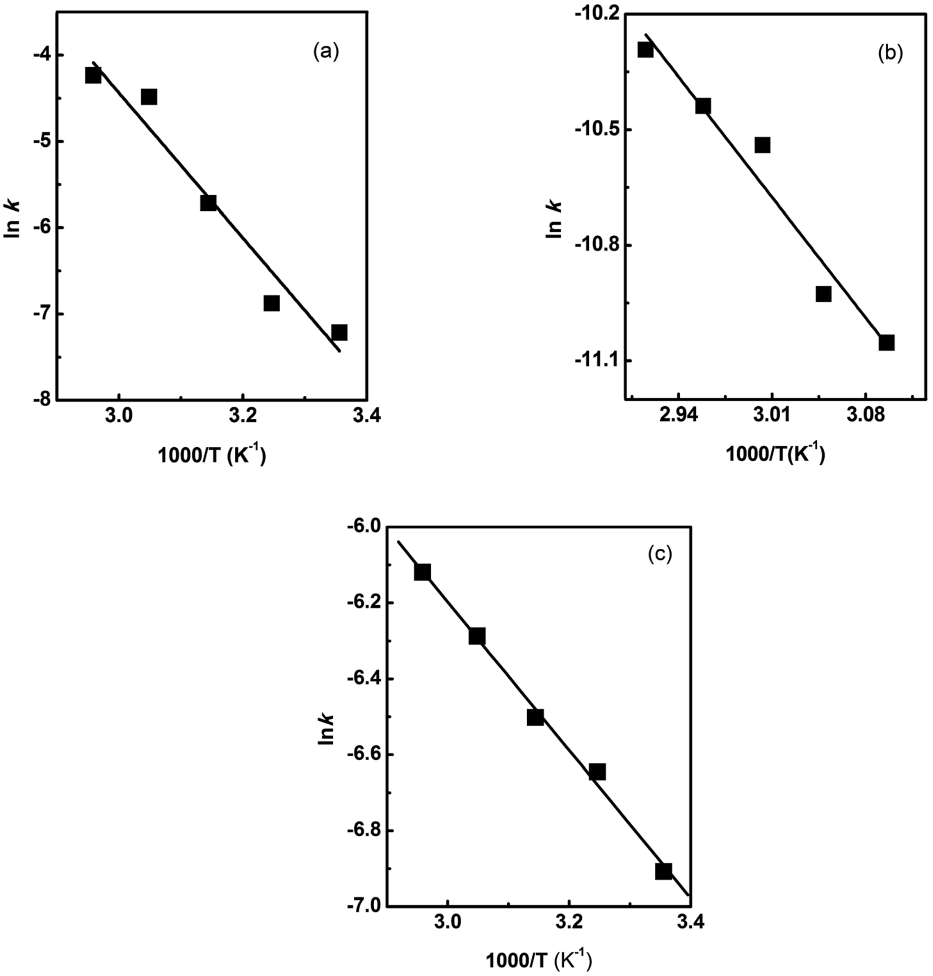


Fig. 4 Arrhenius plots (ln *k versus* 1/*T*) for the reaction of *p*-nitrobenzaldehyde, **1** and methyl acrylate, **2** with DABCO in ionic liquids in (a) [OPy][HSO_4] (b) [OPyr][HSO_4] and (c) [Pyr][HSO_4].

where α is the hydrogen bond donation, β is hydrogen bond accepting tendency (basicity) and π^* is the dipolarity/polarizability tendency. In the case of reactions the equation can be written as:

$$\log k_{\text{obs}} = \log k_0 + a\alpha + b\beta + c\pi^* + \text{other parameters}$$

We have made attempts to correlate reaction rate constants with solvatochromic parameters. At first linear regression was done followed by multiple regressions. The rate constants were also separately fitted with the individual α, β and π^* parameters. The plots are given in Fig. 5(a)–(c). The correlation coefficient very clearly exhibited the dependency of k_2 on β value. Application of the monoparametric equation does not offer satisfactory results. The resulting correlation, obtained by multiple regression, is significant although with some scatter gave the coefficient values as follows:

$$\log k_{2\text{cal}} = -8.581 + 1.069 \times \alpha + 6.022 \times \beta - 0.325\pi^* \ (r^2 = 0.997)$$

All the parameters appear to be important here. However contribution of α and π^* is comparatively negligible as shown by regression values. Interestingly the contribution of β is dominant in affecting the rate of the reaction. The magnitude of coefficient of β indicates a good degree of interaction between the anions of ionic liquids and the substrate. Upon plotting the log k_2 values calculated from equation and experimental k_2 values, solvation pattern as shown in Fig. 5(d) is obtained. The correlation thus obtained between log $k_{2\text{exp}}$ and log $k_{2\text{cal}}$ is fairly satisfactory, where $k_{2\text{exp}}$ and $k_{2\text{cal}}$ are the experimental and calculated k_2 values.

Table 2 Activation parameters for the reaction of *p*-nitrobenzaldehyde, **1** and methyl acrylate, **2** with DABCO in ionic liquids

S. no.	Ionic liquids	$E_a^{\neq}$ (kJ mol^{-1})	$\Delta^{\neq}H$ (kJ mol^{-1})	$\Delta^{\neq}S$ (J mol^{-1} K^{-1})
1	[Pyr][HSO_4]	16.30	13.70	−256.20
2	[Opyr][HSO_4]	129.51	126.74	92.11
3	[Opy][HSO_4]	69.95	67.31	−80.76

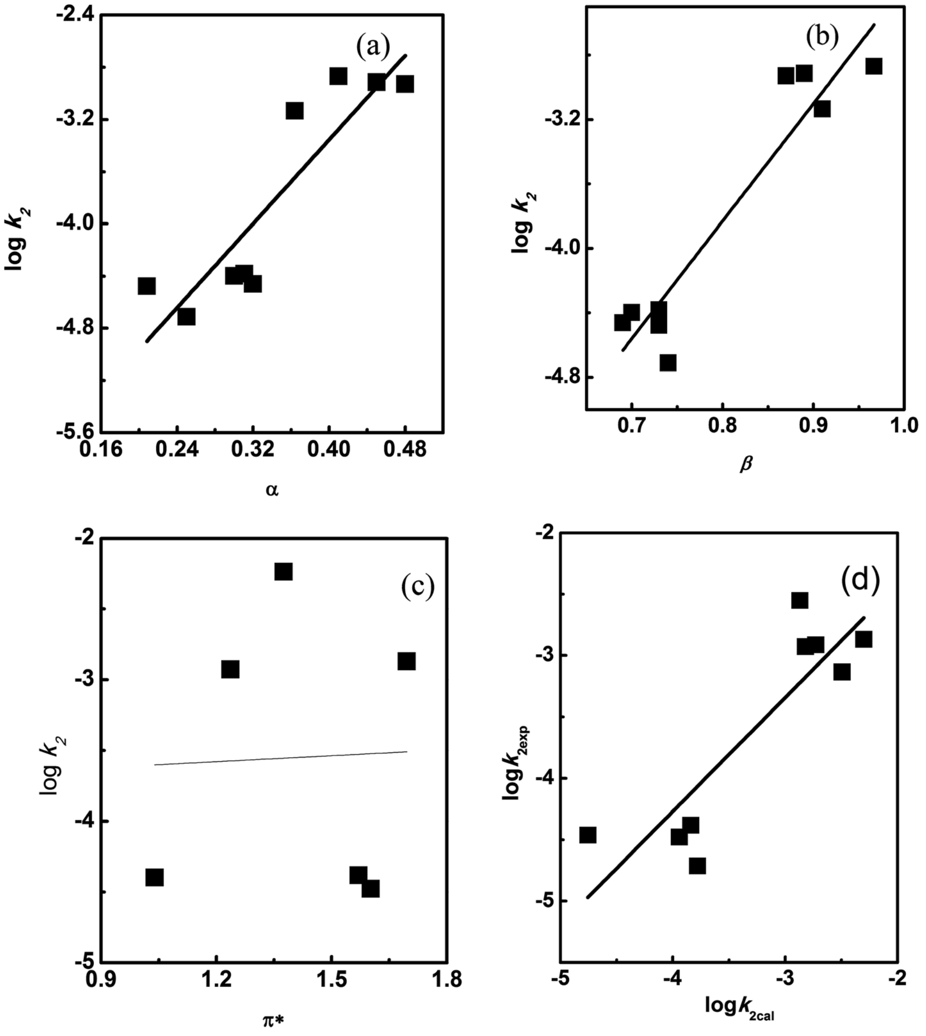
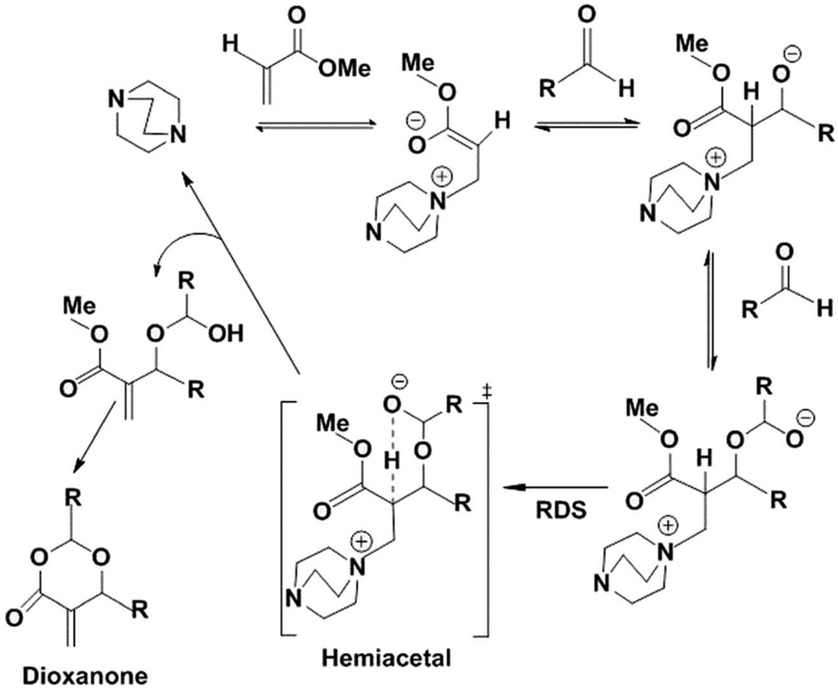


Fig. 5 The plots of log k_2 *versus* (a) α, correlation coefficient = 0.774 (b) β, correlation coefficient = 0.876 and (c) π^*, correlation coefficient = −0.248 (d) correlation of the log of calculated and experimental k_2 values for the reaction of *p*-nitrobenzaldehyde, **1** and methyl acrylate, **2** with DABCO in ionic liquids.

Mechanism of the reaction

The above studies show the predominance of the role of the anion of ionic liquids in catalysing the Baylis–Hillman reaction. A minor role is played by α whereas π^* plays insignificant role. Biparametric equation itself contributes significantly to the rate constants with β playing an important role Increase in the alkyl chain length only increases the activation energy of the reaction. It has no appreciable effect on the order of the reaction. However, the presence of HSO_4^- as anion does affect the mechanism of the reaction. As HSO_4^- ion has a high β value,[34] henceforth it can considerably affect the mechanism and kinetics of the Baylis–Hillman reaction. In 2005, McQuade and co-workers have reported second order dependence of rate of Baylis–Hillman reaction on aldehyde concentration. Solvent like DMSO which has a high β value (0.743) was very effective in driving the reaction to a new pathway which was different to the one proposed by Hill and Isaacs. There results were in complete agreement based upon competitive experiments, kinetic study and rate law equations. Based upon the experimental observations presented here we also propose a similar mechanism in ionic liquids which is exclusively ‘anion dependent’. The steps involved are (a) the reversible Michael addition, involving the attack of DABCO on activated alkene to form an enolate which is a zwitterionic species (b) the attack of enolate on the first equiv. of aldehyde in order to give second zwitterionic species (c) attack of second zwitterionic species on another equiv. of aldehyde leading to the formation of a hemiacetal intermediate (d) transfer of a proton from the α-position of C–H bond to the alkoxide (RDS) and (e) elimination of base with the formation of product. The electron rich species such as DMSO and HSO_4^- ion when present in the reaction medium can destabilize the negative charge present on the alkoxide oxygen. These species solvate only cation making negative charge highly reactive and bare for attack. The developed negative charge tries to satisfy itself by proton transfer from α-carbon. Unfortunately, this transfer leads to an unstable 4-membered transition state. Such proton transfer is geometrically unfavourable too. The presence



Scheme 3 Mechanism of Baylis–Hillman reaction proposed by McQuade and co-workers.

of high charge density on DMSO and HSO_4^- ion further makes the 4-membered transition state unstable. The species then attacks another equivalent of *p*-nitrobenzaldehyde to form a highly stable 6-membered transition state. The proton transfer from α-carbon to alkoxide ion is now energetically favourable. This attack generates hemiacetal intermediate. Rest of the step is the same as elimination of base and product formation. The results give a insight into the mechanistic pathway of the reaction and quite interestingly suggests that HSO_4^- and $MeSO_4^-$ based anion follows McQuade pathway with two equivalents of aldehyde in the rate determining step of reaction (Scheme 3) and other anion based ionic liquids follows Hill and Isaacs pathway with only one equivalents of aldehyde present in the rate determining step of the reaction.

Conclusion

In conclusion, we have used kinetic experiments to demonstrate that the mechanism of the Baylis–Hillman reaction is not unique for all ionic liquids. The nature of the anion of ionic liquids and its basicity can be a very important determinant factor in deciding the pathway of the reaction. The sulfate based ionic liquids are very peculiar in their behaviour since they are the only anions which have two equivalents of *p*-nitrobenzaldehyde participating in the rate determining step of the reaction. Other anions based ionic liquids, when employed have only one equivalent of *p*-nitrobenzaldehyde participating in the rate determining step of the reaction. The valid mechanism in ionic liquids, under investigation, can be a function of the β value of the anion of ionic liquid. The role of the solvent in the kinetics and the rate of reaction has been further confirmed by the Kamlet–Taft based LSER approach. It has been found that the choice of the best parameter for every type of interaction is very crucial because of the complexity of the reaction medium and also because of their susceptibility towards more than one facets of the undergoing reaction. Kamlet–Taft based LSER approach also show that Baylis–Hillman reaction exhibits anion dependency. The correlations are best explained by the high basicity of the anions of ionic liquids involved. It has been shown that both rate constant and mechanism of Baylis–Hillman reaction shows dependency on more basic anions. In short, it has been demonstrated here that the ionic liquids with more basic anions follow McQuade mechanism and ionic liquids with less basic ones follow Hill and Isaacs mechanism.

Acknowledgements

AS is thankful to UGC, New Delhi for an award of a Senior Research Fellowship to her. AK is grateful to Department of Science & Technology, New Delhi for awarding him a J. C. Bose National Fellowship (SR/S2/JCB-26/2009).

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