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An Acidity Scale of 1,3-Dialkylimidazolium Salts in Dimethyl Sulfoxide Solution

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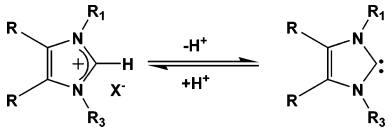
HIn = indicator acid

Equilibrium acidities of 16 1,3-dialkylimidazolium-type ionic liquid (IL) molecules (**1**−**16**) were systematically measured by the overlapping indicator method at 25 °C in dimethyl sulfoxide (DMSO) solution. The pK_a values were observed to range from 23.4 for IL **12** to 19.7 for IL **6** (Tables 1 and 2), responding mainly to structural variations on the cation moiety. Excellent agreement between the spectrophotometrically determined pK_a and that derived from NMR titration for 1,3,4,5-tetramethylimidazolium bis(trifluoromethanesulfonyl)imide (**12**) and the close match of the obtained pK values with the reported data in literature provide credence to the acidity measurements of the present work. The substituent effects at the imidazolium ring and the effects of counterions on the acidities of ionic liquids are discussed.

In recent years, the room temperature ionic liquids (RTILs) have become a fascinating new class of "greener" alternatives to volatile organic solvents that are characterized by their favorable properties such as liquidity over a wide range of temperatures, negligible vapor pressure, low flammability, good thermal stability, high conductivity, and so on.[1] Among the common RTILs developed, the imidazolium-type ionic liquids derived from 1,3-dialkylimidazolium cations in association with weakly coordinating anions represent the most popular and have recently found many applications in electrochemistry,[2] polymer chemistry,[3] organic and inorganic synthesis,[4] and separation[5] and catalytic[6,7] processes. In these cases, the imidazolium ILs were normally used as "inert solvents" under acidic,[6] neutral,[7] and basic[8] conditions. However, recent investigations started to accumulate increasing examples of the "non-innocent" nature[9] of the imidazolium ILs and therefore suggest an immediate demand for more fundamental studies on the stability of this type of new reaction media under harsh conditions.

SCHEME 1. Formation of *N*-Heterocyclic Carbene by Deprotonation of Imidazolium Ionic Liquid



The instability of the imidazolium ILs stems mainly from the relatively high acidity of the C2 hydrogen in the cation moiety.[17] This property of the imidazolium cations may, on the other hand, lead to formation of the *N*-heterocyclic carbenes (Scheme 1)[10] that have recently been found to promote a wide range of applications in organometallic catalysis[11] and a number of important reactions such as benzoin condensation[12] and acyl transfer.[13] However, the base-sensitive C2 hydrogen may also cause unexpected side reactions[14] and thus defines a borderline-window for imidazolium ILs to be used as reaction media. The promising prospects of the RTILs and *N*-heterocyclic carbenes in modern organic synthesis thus raise two important fundamental questions for deeper understanding of their properties: (1) How acidic is the C2-hydrogen of imidazolium IL, or in other words, how stable is its conjugate base *N*-heterocyclic carbene under basic conditions? (2) How does the substituent variation at *N*- and C(4,5)-positions of the imidazolium cation ring affect the C−H acidity (or the *N*-heterocyclic carbene stability)?

There have been only a few reports on the acidities of imidazolium salts (or basicity of imidazol-2-yl carbenes) in the literature up to the present.[15,16] Alder et al. measured the pK_a

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of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene as 24.0 in DMSO-d_6 by the NMR method.[15] Kim and Streitwieser reported a DMSO pK_a for a slightly different species 1,3-di-*tert*-butylimidazol-2-ylidene as 22.7.[16] Recently, Amyes and co-workers estimated a few aqueous-phase kinetic acidities for simple imidazolium cations by the deuterium exchange method.[17] Yates et al. predicted the basicity of some nucleophilic carbenes by theoretical computation.[18]

Despite this important progress, fundamental acidity studies of imidazolium cations are, nevertheless, very rare and still remain in urgent need. Besides, most of the previous attention was placed on the imidazolium ion itself and the acidity data were not derived from a normalized medium. It is therefore important to investigate the stability of the commonly used 1,3-dialkylimidazolium ionic liquids under basic conditions and to make the acidity measurements in a single solvent for the purpose of meaningful comparison. This has stimulated us to carry out more inclusive acidity measurements and a structural study of the popular ILs in DMSO solution. Here we wish to report the equilibrium acidities of a family of 16 1,3-dialkylimidazolium-type ILs in DMSO at 25 °C and the structural effects on the stability of their conjugate bases, i.e., the corresponding *N*-heterocyclic carbenes.

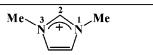
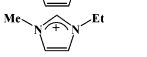
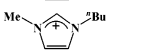
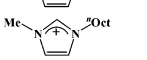
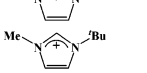
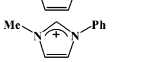
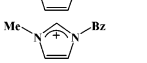
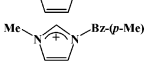
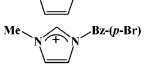
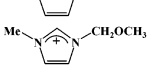
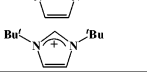
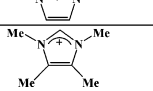
The overlapping indicator method used in this work measures the differences of the equilibrium acidity (pK_a) of an "unknown" acid relative to that of an "indicator" acid (whose pK_a is known) by monitoring the changes of UV/vis absorption of either the indicator or the unknown acid during titrations of one acid to the other under standard conditions.[19] The "absolute" equilibrium acidity of the unknown acid can then be calculated according to the following equations:

$$\mathrm{HA} + \mathrm{In}^- \overset{K_{eq}}{\rightleftharpoons} \mathrm{HIn} + \mathrm{A}^- \quad (1)$$

$$\mathrm{p}K_{HA} = \mathrm{p}K_{HIn} - \log K_{eq} = \mathrm{p}K_{HIn} - \log([\mathrm{HIn}][\mathrm{A}^-]/[\mathrm{In}^-][\mathrm{HA}]) \quad (2)$$

First, the pK_a range of the 1,3-dialkylimidazolium ionic liquids in DMSO was bracketed to be between 17.9 and 25.6 by using two indicator anions with pK_{HA} of 17.9 (9-phenylfluorene)[19] and 25.6 (1,3,3-triphenylpropene),[20] respectively. It was then narrowed down to be around 20−22, using an indicator anion with pK_{HA} = 22.6 (fluorene).[19] For acidity measurement of individual ILs, two carefully selected indicators were used for each ionic liquid. To ensure the most reliable results, the indicators were selected in such a way that their pK_{HA} values should be close enough (<2 pK units) to the presumed value of the ionic liquid of interest. The equilibrium acidities determined for 16 1,3-dialkylimidazolium-type ionic liquids (and analogs) in DMSO under standard conditions along with the indicators used in each measurement are summarized in Tables 1 and 2.

TABLE 1. Equilibrium Acidity Measurements for 1,3-Dialkylimidazolium Ionic Liquids in DMSO at 25 °C

No.	Cations of ILs [a]	HIn (pK_{HIn})[b]	pK_{HA}[c]	pK_a[d] (Assigned)	Runs[e]
1		FH (22.6) 2,3-BenzoFH (23.1)	22.01±0.04 22.02±0.04	22.0	5
2		FH (22.6) 2,3-BenzoFH (23.1)	22.10±0.02 22.08±0.04	22.1	5
3		FH (22.6) 2,3-BenzoFH (23.1)	22.05±0.03 22.01±0.04	22.0	4
4		FH (22.6) 2,3-BenzoFH (23.1)	22.05±0.05 22.08±0.03	22.1	6
5		FH (22.6) 2,3-BenzoFH (23.1)	22.59±0.03 22.59±0.04	22.6	5
6		Carbazole (19.9) CNAH (18.9)	19.74±0.02 19.66±0.02	19.7	5
7		Indole (20.95) Carbazole (19.9)	21.54±0.03 21.60±0.03	21.6	5
8		Indole (20.95) Carbazole (19.9)	21.63±0.01 21.56±0.04	21.6	5
9		Indole (20.95) Carbazole (19.9)	21.18±0.02 21.34±0.02	21.2_5	5
10		Indole (20.95) Carbazole (19.9)	20.54±0.03 20.49±0.03	20.5	3
11		FH (22.6) 2,3-BenzoFH (23.1)	23.27±0.01 23.24±0.04	23.2_5	5
12		FH (22.6) 2,3-BenzoFH (23.1)	23.42±0.02 23.38±0.01	23.4	4

[a] The counterion is bis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2N^-$. [b] The indicators (HIn) are FH, fluorene; 2,3-BenzoFH, 2,3-benzofluorene; and CNAH, 4-chloro-2-nitroaniline. [c] Measured in DMSO by overlapping indicator method as reported previously.[19] [d] The assigned pK_a value is the average of pK_{HA} values. [e] Number of the separate experimental measurements.

TABLE 2. Equilibrium Acidity Measurements for 1-*n*-Butyl-3-methylimidazolium Ionic Liquids with Different Counterions in DMSO at 25 °C

no.	counterion[a]	HIn (pK_{HIn})[b]	pK_{HA}[c]	pK_{ad} (assigned)	runs[e]
3	$(CF_3SO_2)_2N^-$	FH (22.6) 2,3-BenzoFH (23.1)	22.05 ± 0.03 22.01 ± 0.04	22.0	4
13	Cl^-	FH (22.6)	22.01 ± 0.05	22.0	2
14	Br^-	FH (22.6)	22.09 ± 0.01	22.1	3
15	BF_4^-	FH (22.6)	22.12 ± 0.005	22.1	3
16	PF_6^-	FH (22.6)	22.08 ± 0.02	22.1	2

[a] The cation is 1-*n*-butyl-3-methylimidazolium. [b] The indicators (HIn) are FH, fluorene; and 2,3-BenzoFH, 2,3-benzofluorene. [c] Measured in DMSO by the overlapping indicator method as reported previously.[19] [d] The assigned pK_a value is the average of pK_{HA} values. [e] Number of separate experimental measurements.

Effect of Substituents on Equilibrium Acidities. Table 1 shows that the pK_a of ionic liquid **1** in DMSO is 22.0, which is close enough to the previous estimate of the same IL in aqueous solution (23.0) from a kinetic study.[17] The small difference of the acidities in water and in dimethyl sulfoxide is understandable because water is known to solvate (i.e., to stabilize) cations better through hydrogen bonding than nonhydroxylic solvents such as DMSO. In comparison, the solvation difference for the deprotonated product, i.e., the neutral 1,3-dimethylimidazol-2-yl carbene, should be relatively small. The stronger solvated IL **1** in water has to overcome a greater energetic barrier during deprotonation than it does in DMSO and thus resulted in a higher pK_a value. Similar phenomena were also observed previously for the thiazolium cations[21] and for the secondary and tertiary amines.[22]

(17) Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K. *J. Am. Chem. Soc.* **2004**, *126*, 4366−4374.

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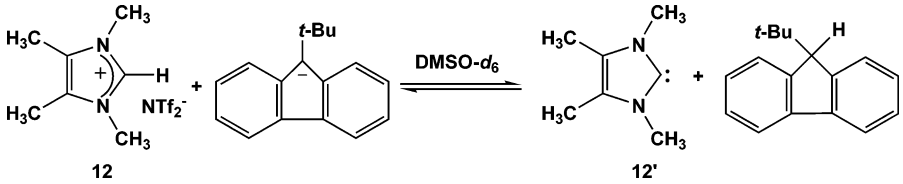
(20) pK_a values for standard hydrocarbon acids in DMSO are taken from: (a) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463. (b) Izutsu, K., Ed. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific Publications: Oxford, UK, 1990.

SCHEME 2. Example for Determination of Acid−Base Equilibrium Constant by ^{1}H NMR Spectroscopy in DMSO-d_6 Solution



Replacement of 1-*N*-methyl in **1** with ethyl, *n*-butyl, or *n*-octyl (to give **2**, **3**, and **4**) did not cause appreciable change on equilibrium acidity ($\Delta pK \leq 0.1$), suggesting that the short or sterically flexible alkyl chains have minimal influence on the solvation of imidazolium cation. On the other hand, substitution of a *tert*-butyl group to the 1-*N* position of **1** (to give **5**) causes a 0.6 p*K* unit decrease in acidity. This can be attributed to the so-called "steric inhibition of solvation" by *tert*-butyl in the deprotonation transition state. This steric inhibition effect can also be found in compound **11** where a second *tert*-butyl group is attached to the 3-*N* position. The effect appears to be additive and causes altogether a 1.2 p*K* decrease in acidity ($pK_a = 23.25$). It is noted that this pK_a for IL **11** is close to but somewhat greater than the value of 22.7 from an equilibrium acidity study of the same compound in the literature.[23]

On the other hand, substitution of 1-*N*-methyl in **1** with phenyl (to give **6**) brought about 2.3 p*K* units increase in equilibrium acidity ($pK_a = 19.7$). The large increase in acidity may be explained by considering a combination of the electron-withdrawing inductive effect of phenyl and the delocalization effect of the phenyl π-system that pulls the p-electron pair at N atoms away from the imidazolium ring and thus makes it less stable.

Table 1 also shows that replacement of 1-*N*-methyl in **1** with a benzyl or *p*-substituted benzyl (to give **7**−**9**) causes an increase in acidity by about 0.4 to 0.75 p*K* unit. The substitution effect is rather small because the aromatic moiety is further apart, but nevertheless, it still reflects a normal type inductive effect of the benzyls. In the same line, the 1.5 units decrease in the p*K* value of **1** by replacing one of the hydrogen atoms at 1-methyl with methoxy (to give **10,** $pK_a = 20.5$) should be easily understandable because of the strong electron-pulling property of the oxygen atom.

In comparison to the rather weak substituent effects of the alkyl substitution at the 1,3-*N* positions of imidazolium ILs (**1**−**11**), further substitution of the hydrogen atoms at C4 and C5 positions with methyl (to give **12**) caused a quite appreciable acid-weakening effect on the C2-hydrogen by as large as 1.4 p*K* units (relative to **1**), due primarily to the cation-stabilizing electron-donating nature of the methyl. This pK_a value of **12** (23.4) derived by the overlapping indicator method agrees very well with a separately measured value of 23.6 of this work by ^{1}H NMR titration (see text below). The 0.2 p*K* unit deviation of the acidity data by the two different methods is reasonable because the NMR pK_a was determined in a more concentrated solution and the high concentration is known to lead to a p*K* measurement greater than normal.[16] Our pK_a value of 23.4 for **12** is also reasonably close to the reported value of 24.0 for an analogous compound, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, measured in DMSO by the NMR method.[15] The 0.6 unit difference may be attributed mainly to the greater electro-donating effect and the "steric inhibition of solvation" effect of the bulky *N*-isopropyl groups, and partially to the concentration effect on the NMR acidity measurement as mentioned previously.

Effect of Counterions. The influence of counterions on the acidity of ionic liquids has not been examined previously in the literature. We therefore measured the equilibrium acidities of 1-*n*-butyl-3-methylimidazolium cation with various counter-anions (ILs **3**, **13**−**16**) as an example of such a study (see data in Table 2). The derived pK_a values of the cation with five different anions are all found to be around 22.1, indicating that the effect of counteranions is essentially negligible. This is not entirely unexpected, however, because previous computational study[24] on the intermolecular interaction energies in the ion pairs of the 1-*n*-butyl-3-methylimidazolium ionic liquids showed that the interaction energies (mainly electrostatic in nature) differ only by a few kilocalories per mole in the absence of solvent and the strong solvation effect in DMSO in the present study may well level off the small differences of interaction energies to the point as observed. The pK_a value of 1,3-dialkylimidazolium-type ionic liquids is thus ultimately dependent on the structure of the cations.

Examination of Acidity Constant of Imidazolium Ionic Liquid in DMSO-d_6 by the NMR Method and Stability of the Corresponding *N*-Heterocyclic Carbenes in Dilute DMSO Solution. A number of excellent literature works have demonstrated that reversible acid−base equilibrium between 1,3-dialkylimidazolium ionic liquid and its conjugate base (imidazol-2-ylidene) can be established in DMSO solution.[15,25] In this work, we examined the acid−base equilibrium of IL **12** with indicator anion 9-*tert*-butylfluorenide in DMSO (Scheme 2) by ^{1}H NMR titration and obtained the acidity constant of IL **12** for the purpose of comparison with the spectrophotometrically determined pK_a data.

The indicator anion 9-*tert*-butylfluorenide ($pK_{HA} = 24.3$)[20] was generated by addition of a DMSO-d_6 solution of potassium dimsyl (about 0.5 equiv) to a DMSO-d_6 solution of 9-*tert*-butylfluorene. Successive additions of a DMSO-d_6 solution of **12** to the resulting indicator anion solution in small aliquots

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(23) The pK_a of this cation was previously measured as 22.7 in DMSO from a reaction of neutral carbene with an indicator acid.[16] This value is 0.55 p*K* unit lower than the pK_a of 23.25 of the present work by the overlapping indicator method, using an indicator anion and imidazolium cation as the starting acid−base pair. The 0.55 p*K* difference still seems to be too large even if the difference in method is taken into consideration. However, as pointed out in ref 16, their pK_a of 22.7 was somewhat underestimated due to ion pair effect. If the ion pair effect was calibrated, the free-ion pK_a would have been corrected to be 23.04, which should be reasonably within the uncertainty range to the pK_a value of the present measurement.

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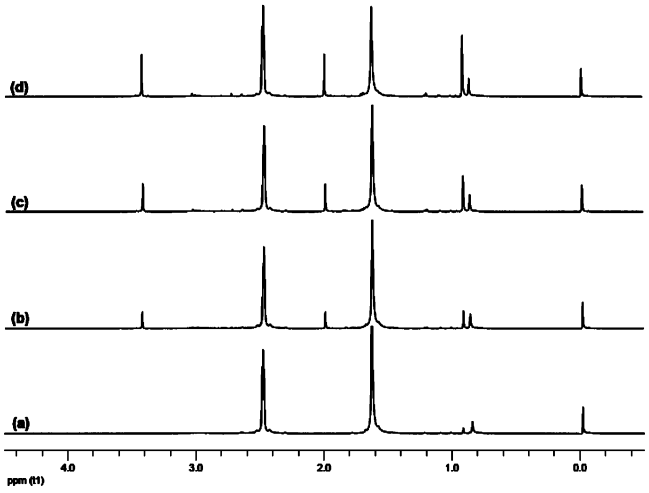

FIGURE 1. Upfield ^{1}H NMR spectra of (a) a mixture of 9-*tert*-butylfluorenide ion and 9-*tert*-butylfluorene; (b) the mixture from a + 0.25 equiv of **12** (to total molar amount of 9-*t*-butylfluorenide ion and 9-*t*-butylfluorene); (c) the mixture from a + 0.50 equiv of **12**; and (d) the mixture from a + 0.75 equiv **12**.

gave mixtures of the four species in Scheme 2 in varying concentrations under equilibrium conditions. The changes of NMR spectrum after each titration are demonstrated in Figure 1 where the signals at δ 3.43, 1.99, 0.91, and 0.84 ppm represent the averages of the *N*-methyl and C(4,5)-methyl protons in IL **12** and in its conjugate base, and the *t*-Bu protons in 9-*tert*-butylfluorene and in 9-*tert*-butylfluorenide, respectively. The ^{1}H NMR signals of the *t*-Bu in 9-*tert*-butylfluorene (δ 0.91) and in its conjugate anion (δ 0.84) were eventually used to evaluate the concentrations of these four species in the established equilibrium. The equilibrium acidity of **12** thus derived from eqs 1 and 2 on the basis of NMR titration is 23.6 $\pm$ 0.1, which agrees very well with the pK_a of the same compound determined by the overlapping indicator method (see above).

The acidity data of RTILs obtained in the present work may, on the other hand, be regarded as a direct measure of the stability of the corresponding *N*-heterocyclic carbenes that are derived from deprotonation of the 1,3-dialkylimidazolium salts. The results indicate that these *N*-heterocyclic carbenes (imidazol-2-ylidenes) are quite stable in dilute DMSO solution at least during the time scales of the NMR and UV titrations. There were no observable changes in the ^{1}H NMR spectra of the acid−base mixture solutions after standing about half an hour at rt, indicating that dimerization[26] and side reaction with the precursor imidazolium salts[27] found in the literature were minimal under our experimental conditions.

To sum up, the equilibrium acidities of 16 1,3-dialkylimidazolium-type ionic liquids in DMSO solution have been successfully determined in this work that provide a scaled measure for both the stability of the imidazolium-type ionic liquids under basic conditions and the stability of their conjugate base *N*-heterocyclic carbenes. Substituent effect on acidity was examined, and it demonstrated that the ring substitution has quite a significant influence on acid−base equilibria with a pK_a span of 19.7−23.4. In contrast, the influence of simple counterions on acidity was shown to be minimal. The observed variations of pK_a with the ring substitution are understandable in terms of the electronic effects and steric inhibition of solvation effect of the substituents.

Experimental Section

Ionic liquids (IL **1**−**16**) were synthesized according to the literature and were dried at 70 °C for 3 h under reduced pressure before used. Indicator compounds were either purchased from a commercial supplier or synthesized in this laboratory. DMSO-d_6 solutions of IL **12** and 9-*tert*-butylfluorenide ion used in ^{1}H NMR titration were prepared in the NMR tubes directly in the glovebox.

Determination of pK_a. The procedures for purification and preparation of the DMSO solvent, the potassium dimsyl base, the solutions of the indicator, and ionic liquids, as well as the overlapping indicator method for pK_a determination as described in details by Bordwell and co-workers,[19] were closely followed in the present work. The concentrations of the indicator and ionic liquid solutions were about 50 mmol/L. The concentration of the potassium dimsyl solution was determined internally as a part of the manipulation during each run. Details of the experimental operation are described in the Supporting Information.

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Note Added after ASAP Publication. There were errors in the structures in the Abstract graphic and Schemes 1 and 2 in the version published ASAP August 29, 2007; the corrected version was published ASAP September 6, 2007.

Supporting Information Available: Preparative procedures, characterization data, and copies of ^{1}H and ^{13}C NMR spectra for 1,3-dialkylimidazolium ionic liquids (IL **1**−**16**), and details of experimental operation and absorption spectra of the model titration process. This material is available free of charge via the Internet at http://pubs.acs.org.

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