

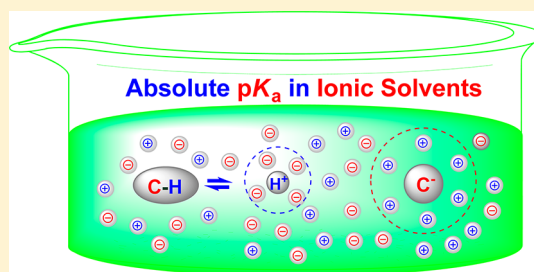
Standard pK_a Scales of Carbon-Centered Indicator Acids in Ionic Liquids: Effect of Media and Structural Implication

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S Supporting Information

ABSTRACT: Energetics of bond dissociation, especially the R–H bond heterolysis free energy (pK_a), has played a central role in promoting chemistry to become a rational science. Despite the oceans of acidity studies in the literature, the current knowledge is limited to that in the classical molecular solvents and is unable to be extended to anticipate the acidity changes in ionic media. As the latter is now very popular for replacing volatile organic solvents, it becomes highly desirable to know how the driving force of bond cleavage is varied as the medium composition is switched from neutral *molecules* to the charged *ions*. Here we describe a general approach to measure absolute pK_a 's in pure ionic liquid (IL). The standard conditions warranting accurate measurement were outlined. The pK_a 's of the selected 18 C–H type indicator acids in four ILs were determined and a convenient indicator platform was constructed for easy expansion of acidity scales. These absolute pK_a 's make possible, for the first time, direct comparisons of bond energies in IL with those in molecular solvent and in the gas phase and should be able to serve as the standard parameters for calibrating computational methods suitable for the studies in ionic media. The effect of cation and anion in IL in relation to structure was analyzed.



INTRODUCTION

The most fundamental process in chemistry, as well as in many areas of biology, is the cleavage and formation of covalent bonds. Bond dissociation energy, as generally affected by media, is the key factor to determine the ease or difficulty of such processes. Because most compounds are stable by nature with high bond strength, chemists have devoted enormous effort to search for various ways to activate the bonds to promote chemical reactions. In the past decade alone, three Nobel prizes in chemistry (in 2001, 2005, and 2010) were awarded to the most successful methodologies of bond activation in solution. Logically, the knowledge of bond energies in various media, which could serve as a quantitative basis for rational designs of bond reorganization, has always been the core concept in chemistry. The ionization constant pK_a , which describes the free energy change of $R-H \rightarrow R^- + H^+$ bond-heterolysis in solution,¹ is the crucial parameter in this regard because many bond transformations involve initially breaking an R–H bond² and evaluation of other modes of bond cleavage energies in solution (e.g., BDE, C–C and C–M bonds, etc.) also relies on pK_a values.³

Many pK_a scales have already been reported,^{4–7} but these works focused almost entirely on molecular solvents, with only a few cases on Brønsted acidity in ionic liquid (IL) appearing recently.⁸ Most of these previous works on IL acidities provided *relative* values of narrow span (~ 2 pK units), however, and the measurements were largely carried out in the presence of certain molecular additives. Very recently, Doherty et al. reported the first absolute pK_b of N-centered bases in ILs by electrochemical approaches.^{8c} Nevertheless, fairly large un-

certainties of the measurements (± 0.4 – 1.0 pK_a) and limitation for substrates other than amines were notified. In fact, there is no general approach reported for accurate measurement of absolute pK_a 's in pure ionic liquid until now.

Ionic liquids, as a popular category of reaction media for substituting volatile organic solvents,⁹ have found many applications in chemistry, biology, and industry.¹⁰ As bond energetics is critically important to the chemistry and biology in ILs and there is no way yet to obtain intrinsic and absolute bond data in ILs, some basic questions are immediately raised, such as, can we use the existing knowledge of bond heterolysis free energies obtained in molecular solvents, e.g., the pK_a 's in water or in DMSO, to assess the strength of a bond in ionic media? Or, would it be possible to apply some physical parameters already measured in ionic liquid, such as dielectric constants or spectral data or else, to estimate the extent and the direction of the effect introduced by switching the medium composition from molecules to ions on bond energy? Unfortunately, no obvious solution can be found for these questions based on current knowledge framework.

We have previously explored several experimental approaches to study fundamental bond energetics in molecular solvents.¹¹ The above situation triggered us to originate this fundamental research on bond energetics in ionic media in order to tackle the gaps left in the knowledge framework and to renew our understanding on the effect of media. In particular, here we focused first on the C–H bond heterolysis energies in

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Scheme 1. (A) Typical Acid–Base Equilibrium Involved in pK_a Evaluation. (B) Trans-Metalation Frequently Encountered When Using the Overlapping Method

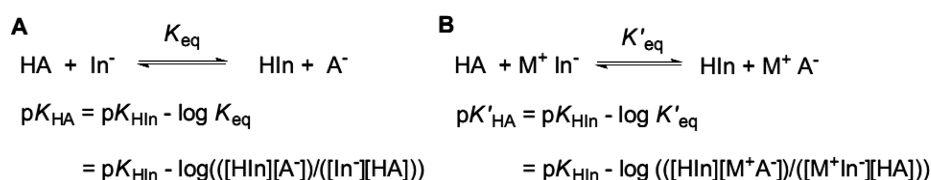


Table 1. Absolute Equilibrium Acidities in Ionic Liquids

	acid ^a	pK_a (BmimOTf) ^b	pK_a (BmimNTf ₂) ^b	pK_a (BmpyNTf ₂) ^b	pK_a (Bm ₂ imNTf ₂) ^b
1	9-EtSO ₂ Fl	17.4	20.3	20.2	21.1
2	PhSO ₂ CH ₂ CN	16.7	19.1	19.4	19.9
3	PhSO ₂ CH ₂ SO ₂ Ph	16.4	18.8	19.2	19.9
4	9-PhSO ₂ Fl	16.4	19.2	19.2	20.0
5	CH ₂ (CN) ₂	16.3	18.9	19.2	19.6
6	9-COOMeFl	15.3	18.3	18.4	19.2
7	PhCOCH ₂ CN ^c	14.3	17.0	17.6	18.2
8	9-CNFl	13.8	16.7	16.6	17.4
9	9-(<i>p</i> -MePhSO ₂)-2-PhSO ₂ Fl	13.8	16.6	16.4	17.1
10	<i>p</i> -ClPhCOCH ₂ CN	13.7	16.4	17.0	17.5
11	9-(<i>p</i> -BrPhSO ₂)-2-PhSO ₂ Fl	13.3	16.1	16.0	16.5
12	<i>p</i> -OMePhCH(CN) ₂	11.1	13.7	13.8	14.3
13	9-CF ₃ SO ₂ Fl	10.0	12.7	12.6	13.2
14	PhCH(CN) ₂	9.8	12.5	12.6	13.0
15	<i>p</i> -ClPhCH(CN) ₂	8.9	11.5	11.7	12.0
16	<i>p</i> -CF ₃ PhCH(CN) ₂	7.5	10.1	10.2	10.4
17	<i>p</i> -CNPhCH(CN) ₂	6.4	8.8	9.1	9.2
18	<i>p</i> -NO ₂ PhCH(CN) ₂ ^d	5.1	7.6	8.0	8.1

^aFl, fluorene. ^bIn pK units; standard deviations: $\leq \pm 0.05 pK$. ^cThe pK_a 's of PhCOCH₂CN measured in the presence of cryptand 222 (1:1 ratio to [K⁺]) under the same conditions are 14.31 in BmimOTf, 17.01 in BmimNTf₂, 17.62 in BmpyNTf₂, and 18.21 in Bm₂imNTf₂, respectively. ^dThe anchor compound, whose pK_a 's were measured on the basis of its self-dissociation in each ionic liquid.

ionic liquid, i.e., the absolute pK_a 's, because until now, no C–H acidities, which constitute the majority of the pK_a databank of organic compounds in DMSO, have been investigated in RTILs. One should realize that the development of the pK_a methodology in molecular media required a great deal of effort;^{4–7} a corresponding development for measuring the standard data in ILs, which has its own unique problems, has not been reported. We now present the first absolute pK_a scales of carbon acids in four ILs measured under standard conditions which are suitable for serving as the indicator basis to build the extended pK_a scale in ILs. We also demonstrate how the standard pK_a 's are used to analyze fundamental problems.

RESULTS AND DISCUSSION

General Strategy. In order to set a common ground for easy expansion of the pK_a scales in ILs for various purposes in future, we have selected 18 fluorene (Fl) and methane derivatives for this study because these C–H acids cover a quite broad pK_a range in DMSO and their role as indicators or standard acids in building up the pK_a scales in molecular solvents were well recorded.⁵ On the other hand, the ILs in this work were imidazolium- and pyrrolidinium-based ionic liquids with NTf₂[−] (bis(trifluoromethanesulfonyl)imide) and OTf[−] (trifluoromethanesulfonate) as counteranions. These ILs differ either in their cation moiety or in anion moiety so that the acidifying effect of both the cation and anion of ILs on the C–H acidity can be examined. Moreover, the pK_a measurement requires the ILs to be highly transparent, pure, nonviscous, and sufficiently stable in the course of acid–base titrations. The four

ILs, i.e., BmimNTf₂, BmpyNTf₂, Bm₂imNTf₂, and BmimOTf (Bmim⁺ = 1-butyl-3-methylimidazolium, Bmpy⁺ = *N*-butyl-*N*-methylpyrrolidinium, Bm₂im⁺ = 1-butyl-2,3-dimethylimidazolium), were found to satisfy these basic requirements and so were synthesized and used as the media of this study.

The pK_a 's in ILs were evaluated by the indicator overlapping strategy. The details of the measurement are described in the Experimental Section. As shown in Scheme 1A, a solution of an indicator (HIn) containing a known concentration of its colored anion ([In[−]]) is titrated with a solution of an acid (HA) to establish an acid–base equilibrium (K_{eq}). The concentration changes of the indicator anion upon additions of the acid solution in aliquots are monitored by UV–vis. The equilibrium acidity of the acid (pK_{HA}) can then be calculated based on the K_{eq} value and the pK_{HIn} of the chosen indicator.

Criteria for Standard Measurement of Bond Heterolysis Energy (pK_a) in Ionic Liquid. Besides the general requirements for regular physicochemical parameter measurement, such as temperature, pressure, etc., that are easy to satisfy, the most critical but easy-to-ignore part of the standard conditions is the medium. To obtain a standard pK_a value that is intrinsic and absolute in nature, the ideal medium should be (1) in high purity, (2) free from ion-pairing complication (as in Scheme 1B), and (3) nondiscriminative in solvation toward both the proton and anion. Failure to follow these guidelines directly causes the results bearing unknown degree of uncertainties. One such case can be found in Scheme 1B.

In this work, the ionic liquids were carefully purified and were used in neat form. A strategy to handle points 1 and 2 was

designed that mainly includes two aspects. First, only the ILs composed of bulky and extensively charge-delocalized cation and anion moieties were selected to prevent the so-called specific ion-associations (SIA) assumed with many ILs, though the universality of SIA is still under much debate. Nonetheless, a recent computation revealing that there are no long-lived ion-pairs in BmimPF₆¹² is in line with our anticipation. Second, the carbanions of the C–H acids studied in this work are all sterically hindered and largely charge-delocalized. This depresses them to ion-pair with the chosen counteranions of large size with delocalized charge. To examine the effectiveness of this strategy in our experiment, a test with cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane),¹³ an excellent K⁺ scavenger, was conducted. It showed that there was basically no change between the pK_a's measured in the presence and in the absence of cryptand 222 (Table 1, footnote c), indicating that perturbations of ion-pairing effect on acidity in IL were minimized under the experimental conditions thus designed. Therefore, the M⁺In⁻ or M⁺A⁻ type of ion-pairing complication as showed in Scheme 1B, the main source of deviations to the obtained pK_a or pK_b as in many previous studies, should not be a serious problem in the present work. Experimental conditions where the SIA is managed to be negligible, as here verified, can be outlined as “standard conditions” that would ensure intrinsic acidity of substrate to be directly measured in ionic liquids. The intrinsic pK_a aimed in this work is highly desirable because the data derived under standard conditions can provide a common standard for scrupulous data analyses and for investigating various effects caused by nonstandard conditions.

It is known that the gas-phase acidity represents the real value of intrinsic acidity. The acidity scales in solution, so long as the data can correlate linearly with the corresponding gas-phase values, can also be regarded as intrinsic, because those pK_a's are able to reflect the intrinsic order of ionization. It may be a surprise to see that, among the most popular pK_a scales used today, essentially only the scale in DMSO was found to exhibit such a feature.¹⁴ In contrast, the correlation of the aqueous-phase pK_a with gas-phase acidity was quite poor because of its prejudicial solvation of water molecule toward different anions. This indicates that it is not always safe to use the scales in water to analyze structural problems because it cannot reflect the exact order of intrinsic property. With this in mind, any arbitrary use of data without distinguishing the suitable range of their applicability (i.e., use them only in the medium where the data were derived, or for analyzing problems within a structurally similar family) is not recommended in order to avoid misinterpretation or misguidance for experiment. The same limitation should also be kept in mind when using the reported relative values in some ILs.^{8a–d}

Establish Absolute pK_a Scale Based on Anchor. One should know that absolute pK_a's are much more useful than relative values because only the absolute data allow direct comparisons of bond energies (i.e., thermodynamic driving forces) between different media or conditions, the key information needed for rational design of reactions. However, the overlapping method showed in Scheme 1 gives a measure of the pK that is relative to the pK_a of the chosen indicator. It means that the absolute pK_a value of the acid (pK_{HA}) can be evaluated only when the absolute pK_a of indicator (pK_{HIn}) is known. But as mentioned above, no such absolute pK_a parameter of any C–H compounds has been measured in pure ionic solvents until now.

In the present work, this has been solved by finding an anchoring pK_a as described in the Experimental Section. That is, if the autoprotolysis constant of a suitable indicator can be directly determined in solution without relying on equilibrating with an added base, this pK_a can be defined as an “absolute” value, and the pK_a's scaled up on the basis of the absolute pK_a of the anchor can constitute an absolute pK_a scale. In this work, we were able to find such an anchor acid, 4-nitrophenylmalononitrile, whose autoprotolysis can be directly monitored in all the ILs of current interest. One should realize that the absolute pK_a thus defined is actually referenced to the solvent. The pK_a's of the anchor are presented in the last entry of Table 1, together with the absolute acidities of other 17 C–H acids measured on the basis of these anchoring pK_a's in four ILs.

With the absolute intrinsic pK_a's in hand, it becomes possible to investigate the effect of various media by using them as the standard. For example, the effect of water in ionic liquid on acidity may be quantified by comparing the standard pK_a with the pK_a's of the same substrate measured under nonstandard conditions with varying amount of the added water. Similarly, the effect of various ion associations may also be elucidated on the basis of comparisons of the standard pK_a's with the data obtained in a “non-standard” system where a particular ion interaction or ion-pairing effect is introduced in a controlled manner. In the following, practices of analyzing the absolute pK_a's in ILs as baseline to probe the effect of structural variations are presented.

Effect of Anion and Cation Moieties on Acidity in Ionic Solvent. Table 1 directly shows that equilibrium acidities of the selected carbon acids cover a range of ~12–13 pK units in the four ILs, which is close to the total measurable range of the pK_a scale in water and is significantly greater than the general coverage of 2–3 pK units reported for relative acidities in ILs.⁸ Thermodynamic scales with broader span of energy (to enable higher resolution) are very useful tools for linear free-energy relationship (LFER) analysis, as represented by Hammett equation and Brønsted equation which are both based on pK_a. Moreover, the initial pK_a scales in ILs established here could be readily expanded by using these C–H acids of known pK_a as indicators to either cover a broader pK range to higher or lower acidities or to measure more compounds that are significant to various types of research.

The most notable feature in Table 1 is that the pK_a of a compound is different in different ILs, demonstrating that the acidifying effect of different IL varies with its composition and structure. For example, the pK_a values of the anchor acid (18) in BmimOTf, BmimNTf₂, BmpyNTf₂, and Bm₂imNTf₂ are 5.1, 7.6, 8.0, and 8.1, respectively. A similar pattern of pK_a variation is observed with others. Further inspection of the data reveals that the pK_a's in BmimOTf are all about 2–3 pK units lower (i.e., more acidic) than those in the other three ILs with NTf₂⁻ as a common anion. This is not difficult to understand because the negative charge in OTf⁻ is more localized on oxygen and the size of OTf⁻ is smaller than NTf₂⁻, causing a stronger solvation (acidifying) effect than its counterpart. Therefore, it is reasonable to expect that a Brønsted acid should be more acidic in an ionic liquid with anions of smaller size and higher proton affinity.

It is also quite interesting to compare the data in columns 2–4 where the ILs share a common counterion NTf₂⁻. Though the changes in pK_a brought by varying the structure of the cationic part of the IL are relatively small as compared to the effect of its counteranion, they are meaningful and worth

noting. As shown, the general trend of pK_a change is $Bm_2imNTf_2 > in BmpyNTf_2 > in BmimNTf_2$ for all aliphatic carbon acids, suggesting an opposite order of the respective cations to solvate the corresponding carbanions. This order may be understood by considering the steric and delocalization effects of the cation. Since $Bmim^+$ is the least hindered cation among the three under comparison, so it is expected to solvate carbanion better than the other two.¹⁵ The slightly higher pK_a value in Bm_2imNTf_2 than in $BmpyNTf_2$ could be attributed to the better delocalization of the positive charge in Bm_2im^+ than in $Bmpy^+$ since the former is centered at sp^2 nitrogen whereas the latter is at sp^3 nitrogen. As for whether or not the hydrogen atom at the $Bmim^+$ ring (C2–H) was involved in stabilizing the very weakly hydrogen-bond-accepting carbanion, it was paid with no specific attention here in this work that focused mainly on establishing the scales, but will be a good subject of future investigation. Nevertheless, the varying acidifying effect of the cations observed here has not been disclosed previously, indicating the importance of carrying out the acidity measurement under strictly controlled conditions. Thus, the above shows clearly that both the cation and anion moieties of the IL, rather than only the anion as known before, can play significant roles in promoting acidic bond dissociation in ionic media. The greater effect of anion on acidity as compared to cation should be due to its stronger solvation toward proton than the solvation of the cation toward carbanion.

Regression Analysis among pK_a 's in Different ILs.

Having shown that standard pK_a 's are indeed a powerful tool to meticulously probe the structural effect of media on bond cleavage free energies (cf. $1\text{ pK} = 1.364\text{ kcal/mol}$), we now turn our attention to linear correlation, which has widely been applied in rational analyses. Specially, this was performed among the pK_a 's in the 4 ILs to examine the relationships between the scales obtained in different ionic media. As shown in Figure 1 (also see Figures S1 and S2 in the Supporting

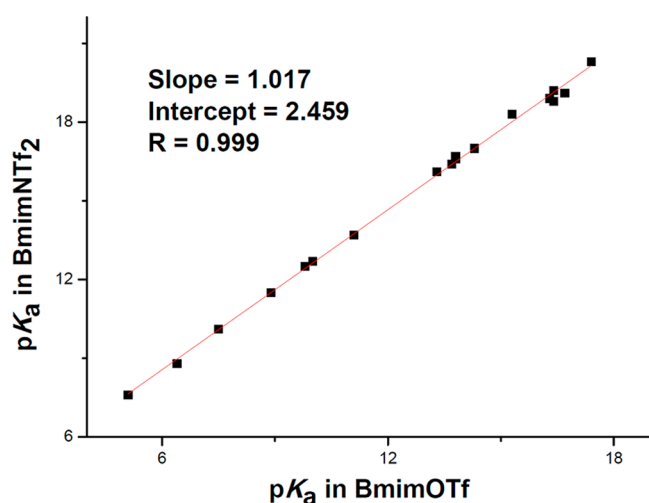


Figure 1. Linear regression between pK_a 's in $BmimNTf_2$ and pK_a 's in $BmimOTf$.

Information), when the pK_a 's in the other 3 ILs were plotted against those in $BmimOTf$, excellent straight lines with slopes close to unity and R of 0.998–0.999 were obtained. These are the first observation of linear correlation of the type.

Comparison of Heterolytic C–H Bond Energies in Ionic Solvent, Molecular Solvent, and the Gas Phase.

The excellent linear correlation between the pK_a 's in different ILs allows us to take the scale in $BmimOTf$ as a representative for the comparison of the heterolytic bond energy (i.e., pK_a) in ILs with those in molecular solvent and in the gas phase. Since the data necessary for the comparison are not all available, only those that allow meaningful comparisons were collected in Table 2.

Table 2. Acidity Data in $BmimOTf$, DMSO,¹⁶ and in the Gas Phase.^{16b,17}

	acid ^a	pK_a ($BmimOTf$)	pK_a (DMSO)	ΔG_{acid}^b (gas phase)
1	9-EtSO ₂ Fl	17.4	12.3	
2	PhSO ₂ CH ₂ CN	16.7	12.0	
3	PhSO ₂ CH ₂ SO ₂ Ph	16.4	12.3	
4	9-PhSO ₂ Fl	16.4	11.6	
5	CH ₂ (CN) ₂	16.3	11.0	328.3
6	9-COOMeFl	15.3	10.4	
7	PhCOCH ₂ CN	14.3	10.2	326.3
8	9-CNFl	13.8	8.3	321.4
9	9-(<i>p</i> -MePhSO ₂)-2- PhSO ₂ Fl	13.8	8.6	
11	9-(<i>p</i> -BrPhSO ₂)-2- PhSO ₂ Fl	13.3	7.7	
12	<i>p</i> -OMePhCH(CN) ₂	11.1	5.7	315.4
14	PhCH(CN) ₂	9.8	4.2	314.3
15	<i>p</i> -ClPhCH(CN) ₂	8.9	3.1	309.0
18	<i>p</i> -NO ₂ PhCH(CN) ₂	5.1	−1.8	299.5

^aFl, fluorene. ^bIn kcal mol^{−1}.

Table 2 makes possible a direct comparison of bond energy, for the first time, among all the three basic categories of reaction media known in chemistry (i.e., molecular and ionic media, gas phase). It clearly shows that the C–H bonds are tremendously more prone to acidic dissociation in solution, no matter ionic or molecular in nature, than in the gas phase, demonstrating the great power of solvation. A closer look further finds that the acid in $BmimOTf$ is about 4–7 pK units weaker than that in DMSO, which provides the first direct comparison between the bond parameters in ionic and in molecular media. This order may not be so easy to anticipate, however, because neither a comparison of their dielectric constants in IL nor computation based on the current knowledge of solvation in molecular solvents can present it straightforwardly.

Regression analysis was also performed for the data in Table 2. It revealed a very good linear correspondence between the pK_a 's in $BmimOTf$ and in DMSO (Figure 2A). This is not surprising since the scales measured in both ILs and DMSO are free from ion-pa-ring perturbation, thereby allowing them to represent the intrinsic acidities of the compounds. Plotting the pK_a 's in $BmimOTf$ versus the gas-phase acidities also results in a good line (Figure 2B), further confirming that the acidity scales obtained in the present ILs are indeed intrinsic in nature.

CONCLUSIONS

Four absolute pK_a scales of the indicator carbon acids in pure ionic liquids have been established. The standard method developed here warrants accurate measurement of the absolute and intrinsic pK_a 's and is not just limited to the C–H bonds. With the pK_a data set of the indicators reported, acidity scales could be readily expanded to include many substrates of

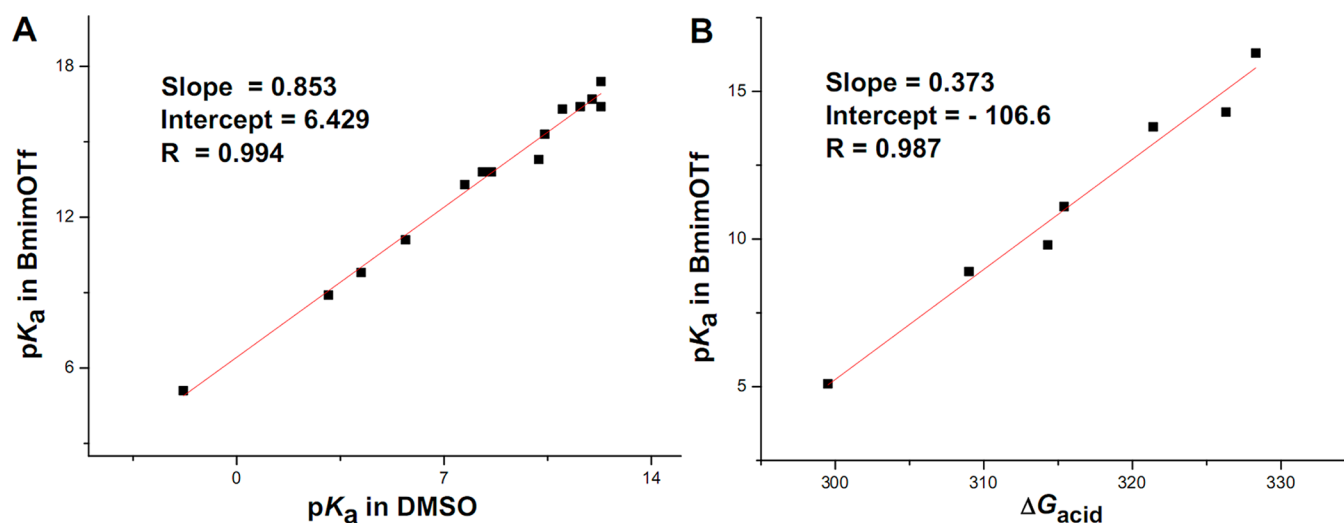


Figure 2. Correlation analyses among acidities in IL, in molecular solvent, and in the gas phase: (A) pK_a 's in BmimOTf vs pK_a 's in DMSO; (B) pK_a 's in BmimOTf vs the gas-phase acidities.

interest. Examples of utilizing these pK_a scales to analyze fundamental problems in ionic liquids such as solvation effect of the cation and anion, relationships among the pK_a 's in different ILs, have been presented. In addition, the absolute pK_a 's may also be used to derive bond energies of other modes of bond dissociation such as BDE and the C–C bond strengths in ionic media. We expect that the standard pK_a should be useful to serve as the quantitative referencing baseline for the development of computational methods that are suitable to study the problems in ionic media in particular. Therefore, the standard pK_a scales in the ILs can provide a powerful platform for studies of many fundamental problems related to bond transformations in an ionic environment.

EXPERIMENTAL SECTION

Materials. Ionic liquids were synthesized and purified based on the literature procedures.¹⁸ The carbon acids 9-ethylsulfonylfluorene,¹⁹ 9-phenylsulfonylfluorene,^{5a} 9-methoxycarbonylfluorene,^{5a} 9-cyanofluorene,^{5a} para-substituted phenylmalononitriles,²⁰ and 1,1-bis-ethanesulfonyl-2-methylpropane²¹ were synthesized and characterized by known methods. Cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane), propanedinitrile, phenylsulfonylacetonitrile, bis(phenylsulfonyl)methane, benzoylacetonitrile, and (4-chlorobenzoyl)acetonitrile were commercially available. Solid substrates and other commercial reagents for synthesis were carefully recrystallized and dried before use. Toluene and ether were distilled from Na. Acetonitrile (AN), ethyl acetate, and dichloromethane (DCM) were distilled from CaH_2 . 1-Methylpyrrolidine, 1-methylimidazole, and 1, 2-dimethylimidazole were distilled from KOH. 1-Bromobutane was distilled from P_2O_5 . By Karl Fischer method, the water content in ionic liquid with NTf_2^- as the anion was 1–2 mmol, and in BmimOTf was 2–3 mmol.

1-*n*-Butyl-3-methylimidazolium Bromide (BmimBr). Freshly distilled 1-bromobutane (300 mL) was added slowly to a well-stirred mixture of 1-methylimidazole (160 mL) and toluene (100 mL). When the addition was completed, stirring was continued at room temperature for 72 h and then at 45 °C for 48 h. The mixture was cooled to room temperature and separated into two layers. The product in the bottom layer was then recrystallized from ethyl acetate/AN five times. The solid was dried for 3 h in vacuo at 60 °C to afford colorless BmimBr (300 g, 68%): 1H NMR (400 MHz, DMSO- d_6) δ 9.41 (s, 1H), 7.91 (s, 1H), 7.83 (s, 1H), 4.23 (t, 2H, $J = 7.16$ Hz), 3.91 (s, 3H), 1.79 (m, 2H), 1.26 (m, 2H), 0.90 (t, 3H, $J = 7.35$ Hz) ppm; ^{13}C NMR (100.6 MHz, DMSO- d_6) δ 137.2, 124.2, 122.9, 49.1, 36.4, 32.0, 19.4, 14.0 ppm.

1-*n*-Butyl-3-methylimidazolium Triflate (BmimOTf). The solution of sodium triflate (172 g) in deionized water (100 mL) was added to a solution of BmimBr (219 g) in deionized water (200 mL). The mixture was stirred at room temperature for 6 h, and extracted with DCM (5 × 50 mL). The combined organic phase was washed with deionized water until bromide free, as determined by silver nitrate test, and dried with anhydrous $MgSO_4$. The viscous liquid obtained by evaporation under reduced pressure was washed with ether, and dried in vacuo at 70 °C for 5 h to give a colorless liquid BmimOTf (236 g, 82%): 1H NMR (400 MHz, AN- d_3) δ 8.61 (s, 1H), 7.43 (s, 1H), 7.38 (s, 1H), 4.14 (t, 2H, $J = 7.31$ Hz), 3.83 (s, 3H), 1.80 (m, 2H), 1.31 (m, 2H), 0.91 (t, 3H, $J = 7.36$ Hz) ppm; ^{13}C NMR (100.6 MHz, AN- d_3) δ 135.9, 123.3, 122.0, 120.8, 48.9, 35.5, 31.3, 18.6, 12.4 ppm.

1-*n*-Butyl-3-methylimidazolium Bis-(trifluoromethylsulfonyl)amide (BmimNTf₂). A solution of BmimBr (91 g) in deionized water (100 mL) was mixed with a solution of lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) (120 g) in deionized water (100 mL). The mixture was stirred at room temperature for 24 h. The same purification procedure was used as for BmimOTf to give a colorless liquid BmimNTf₂ (165 g, 95%): 1H NMR (400 MHz, DMSO- d_6) δ 9.10 (s, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 4.16 (t, 2H, $J = 7.16$ Hz), 3.85 (s, 3H), 1.77 (m, 2H), 1.28 (m, 2H), 0.91 (t, 3H, $J = 7.37$ Hz) ppm; ^{13}C NMR (100.6 MHz, DMSO- d_6) δ 137.1, 124.2, 122.9, 120.1, 49.2, 36.4, 32.0, 19.4, 13.8 ppm.

1-*n*-Butyl-2,3-dimethylimidazolium Bis-(trifluoromethylsulfonyl)amide (Bm₂imNTf₂). The same procedure was used as for BmimBr. From 1-bromobutane (150 mL) and 1,2-dimethylimidazole (90 mL), 1-*n*-butyl-2,3-dimethylimidazolium bromide (Bm₂imBr) was obtained as a white solid (201 g, 86%). A solution of Bm₂imBr (100 g) in deionized water (100 mL) was mixed with a solution of $LiNTf_2$ (123 g) in deionized water (100 mL). The mixture was stirred at room temperature for 24 h. The same purification procedure was used as for BmimOTf to give a colorless liquid, Bm₂imNTf₂ (170 g, 91%): 1H NMR (400 MHz, AN- d_3) δ 7.25 (m, 2H), 4.03 (t, 2H, $J = 7.40$ Hz), 3.69 (s, 3H), 2.50 (s, 3H), 1.74 (m, 2H), 1.34 (m, 2H), 0.94 (t, 3H, $J = 7.39$ Hz) ppm; ^{13}C NMR (100.6 MHz, AN- d_3) δ 144.1, 121.9, 120.5, 119.6, 47.7, 34.4, 31.0, 18.8, 12.4, 8.7 ppm.

1-*n*-Butyl-1-methylpyrrolidinium Bis-(trifluoromethylsulfonyl)amide (BmpyNTf₂). The same procedure was used as for BmimBr. From 1-bromobutane (150 mL) and 1-methylpyrrolidine (104 mL), 1-*n*-butyl-1-methylpyrrolidinium bromide (BmpyBr) was obtained as a white solid (153 g, 69%). A solution of BmpyBr (100 g) in deionized water (100 mL) was mixed with a solution of $LiNTf_2$ (129 g) in deionized water (100 mL). The solution was stirred at room temperature for 24 h. The same purification procedure was used as for BmimOTf to give a colorless liquid

BmpyNTf₂ (177 g, 93%): ¹H NMR (400 MHz, AN-d₃) δ 3.43 (s, 4H), 3.27–3.23 (m, 2H), 2.96 (s, 3H), 2.18 (s, 4H), 1.74 (m, 2H), 1.39 (m, 2H), 0.98 (t, 3H, *J* = 7.39 Hz) ppm; ¹³C NMR (100.6 MHz, AN-d₃) δ 119.6, 64.0, 63.7, 47.8, 24.9, 21.0, 19.0, 12.5 ppm.

2-(Phenylsulfonyl)-9-(*p*-tolylsulfonyl)fluorene (9-(*p*-MePhSO₂)-2-PhSO₂Fl). 2-(Phenylsulfonyl)fluorene was prepared by the method of Aleykuty.²² NBS (2.0 g) and AIBN (30 mg) were added to a solution of 2-(phenylsulfonyl)fluorene (3.2 g) in dry CCl₄ (10 mL). The mixture was stirred at 80 °C until all the solid suspended in solution. Filtration and concentration afforded 9-bromo-2-(phenylsulfonyl)fluorene which was purified by column chromatography.

A solution of 9-bromo-2-(phenylsulfonyl)fluorene (2.1 g) in ethanol (10 mL) was mixed with sodium methoxide (0.32 g) and 4-methylthiophenol (0.74 g). The mixture was refluxed for 2 h and evaporated in vacuo to afford a solid which was then dissolved in DCM. The DCM solution was filtered and evaporated in vacuo to yield 9-(4-methylphenylthio)-2-(phenylsulfonyl)fluorene which was then purified by column chromatography.

9-(4-Methylphenylthio)-2-(phenylsulfonyl)fluorene (1.9 g) was added to a mixture of 30% H₂O₂ (10 mL) and acetic acid (30 mL). Afterward, the solution was stirred at 50 °C for 30 min, cooled, and poured into ice water (200 mL). The precipitate was collected by filtration and then dissolved in DCM. The DCM solution was dried with anhydrous Na₂SO₄ and evaporated to afford a crude product which was purified by column chromatography. Repeated crystallization from DCM/petroleum ether gave white needles (0.76 g, 37%): ¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.09–8.00 (m, 4H), 7.65–7.53 (m, 5H), 7.51–7.43 (m, 2H), 6.75 (d, 2H, *J* = 8.23 Hz), 6.66 (d, 2H, *J* = 8.20 Hz), 5.44 (s, 1H), 2.17 (s, 3H) ppm; ¹³C NMR (100.6 MHz, CDCl₃) δ 146.4, 144.6, 141.9, 140.6, 139.8, 137.0, 136.8, 133.3, 131.2, 129.9, 129.4, 129.0, 128.9, 128.5, 127.7, 127.5, 126.6, 121.0, 120.4, 71.0, 21.5 ppm.

9-(*p*-Bromophenylsulfonyl)-2-(phenylsulfonyl)fluorene (9-(*p*-BrPhSO₂)-2-PhSO₂Fl). 9-(*p*-BrPhSO₂)-2-PhSO₂Fl was prepared according to the procedure of 9-(*p*-MePhSO₂)-2-PhSO₂Fl as white needles (0.79 g, 39%): ¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H), 8.09–8.05 (m, 4H), 7.67–7.56 (m, 5H), 7.53–7.46 (m, 2H), 6.97 (d, 2H, *J* = 8.61 Hz), 6.66 (d, 2H, *J* = 8.59 Hz), 5.46 (s, 1H) ppm; ¹³C NMR (100.6 MHz, CDCl₃) δ 146.3, 141.8, 140.9, 139.8, 136.5, 136.3, 133.4, 133.0, 131.1, 130.4, 130.2, 129.6, 129.5, 129.2, 127.7, 127.5, 126.6, 121.2, 120.6, 70.9 ppm.

9-Trifluoromethylsulfonylfluorene (9-CF₃SO₂Fl). 9-Trifluoromethylsulfonylfluorene was synthesized according to the literature method by Fuchs.²³ *n*-BuLi in hexane (4.8 mL of a 2.5 M solution) was added to a solution of fluorene (2 g) in ether (10 mL) at –78 °C. The mixture was stirred at –78 °C for 1 h. Then triflic anhydride (1.69 g) was added. Afterward, the mixture was quenched with HCl aqueous solution (5%). The aqueous layer was extracted with ether (3 × 10 mL). The combined organic layer was washed with brine, dried, and evaporated in vacuo to afford a crude product which was further purified by column chromatography. Repeated crystallization from ethanol gave white needle crystals (0.94 g, 53%): ¹H NMR (400 MHz, AN-d₃) δ 7.91 (d, 2H, *J* = 7.65 Hz), 7.88 (d, 2H, *J* = 8.17 Hz), 7.60 (t, 2H, *J* = 7.52 Hz), 7.47 (t, 2H, *J* = 8.59 Hz), 6.00 (s, 1H) ppm; ¹³C NMR (100.6 MHz, AN-d₃) δ 141.7, 132.1, 130.3, 127.8, 126.7, 120.5, 119.7, 68.0 ppm. HRFTICR-MS (ES[–]) calcd for [C₁₄H₈F₃O₂S][–] 297.0203, found 297.0207.

1,1-Bis-ethanesulfonyl-2-methylpropane. Trimethylchlorosilane (20 mL) was added dropwise to a stirred solution of isobutylaldehyde (10 mL) and ethanethiol (16.4 mL) in CHCl₃ (70 mL) at 0 °C. The mixture was stirred for 2 h and washed with Na₂CO₃ aqueous solution (5%) and deionized water. The organic phase was dried with anhydrous Na₂SO₄ and evaporated to give a colorless liquid which was further purified by distillation in vacuo. The colorless liquid obtained was added to a solution of 30% H₂O₂ (100 mL) and acetic acid (300 mL). The mixture was stirred at room temperature for 2 h and then at 40 °C for 30 min. After being cooled to room temperature, the solution was poured into ice–water (800 mL). The aqueous solution was extracted with DCM (3 × 200 mL). The combined DCM

phase was washed with deionized water, dried with anhydrous Na₂SO₄, and evaporated in vacuo to afford a crude product. Repeated crystallization from ethanol gave white needle crystals (7.8 g, 29%): ¹H NMR (400 MHz, AN-d₃) δ 4.46 (s, 1H), 3.45 (m, 2H), 3.34 (m, 2H), 2.84 (m, 1H), 1.41 (d, 6H, *J* = 7.10 Hz), 1.37 (t, 6H, *J* = 7.45 Hz) ppm; ¹³C NMR (100.6 MHz, AN-d₃) δ 81.0, 49.0, 28.1, 19.2, 4.6 ppm.

Details of Measurement. All manipulations were carried out under dry argon using standard Schlenk techniques.

Equipment. The indicator and acid reservoirs, pK cell, and syringes for pK_a measurement in ionic liquids are similar to those for the pK_a study in DMSO.^{5a} All weights were recorded to ±0.0001 g, and absorbance was measured with a UV/vis spectrophotometer.

Preparation of the Base. Preparation of the base used for generating carbanions was carried out under dry argon using standard Schlenk techniques. Under the flow of Ar, 2 mL of commercial potassium hydride dispersed in mineral oil was transferred into a 100 mL Schlenk flask. The mineral oil was removed by 3–5 successive washing with 10 mL of dry pentane. The remainder pentane was evaporated in vacuo, and clean KH was obtained. 1,1-Bis-ethanesulfonyl-2-methylpropane (242 mg) was added to a solution of KH (40 mg) in 10 mL of dry THF. The mixture was stirred at room temperature. Then the hydrogen generation was completed in 5 min to give a clear solution. The solution was concentrated in vacuo to give a white solid, which was washed repeatedly with ether (3 × 10 mL) to eliminate unreacted residues and then yielded the desired high quality potassium salt of the base. Next, 4 mL of the corresponding ionic liquid was added to the mixture of this potassium salt in 5 mL ether and was stirred until the salt was all dissolved into the ionic liquid phase. The ionic liquid phase was centrifuged to give a clear solution, and the ether was removed in vacuo. The resulted colorless basic liquid was kept under Ar in the refrigerator and was used as the base for generating carbanions in pK_a measurement.

Preparation of Solutions of Indicators and Acids. Solutions of solid indicators and acids were prepared by weighing ca. 20 mg of compound into the reservoir. The reservoir was then assembled, degassed, and weighed. A desired amount of ionic liquid (usually 2 mL) was added by syringe. The exact amount of ionic liquid was determined gravimetrically.

pK_a Measurement in Ionic Liquids. The pK measurement was started by degassing and weighing the pK cell. The exact amount of all solution added to the cell was determined gravimetrically. Ionic liquid (usually 1.5 mL) and a small amount (20–50 mg) of the base (potassium salt of 1,1-bis-ethanesulfonyl-2-methylpropane carbanion in ionic liquid) was added and the cell weighed. Afterward, the cell was placed in the spectrophotometer at 25 °C, and a baseline was recorded. The solution of an indicator of known pK_a was added in small aliquots to make sure that several points (at least three) could be obtained before the total amount of indicator added exceeded the amount of base present in the cell. Both the spectrum and the weight for each addition were recorded. Plotting the absorbance vs the concentration of indicator gave a perfectly linear correlation with a correlation coefficient better than 0.9999, the slope of which is equal to the extinction coefficient for the indicator anion at the selected wavelength. An excess amount of indicator solution was added to make sure the absence of the base in the cell and then the spectrum was recorded. From the spectrum with excess indicator present, the concentration of the indicator added, and the measured extinction coefficient, the concentrations of the indicator and indicator anion present in the cell could be calculated.

The acid of unknown pK_a was added to the cell in several aliquots. Both the weight and the spectrum were recorded after each addition. From the change in the spectrum, the equilibrium constant *K*_{eq} could be calculated for each addition of acid. Then the pK_a value of the acid was calculated from *K*_{eq} and the known pK_a value of the indicator. The pK_a values measured under standard conditions are usually reproducible to within ±0.05 pK_a unit.

Absolute pK_a of the Anchor Compound in Ionic Liquids. The absolute acidity of the anchor compound 4-nitrophenylmalononitrile in ionic liquid was determined by measuring the equilibrium position of its self-dissociation. This is the key part to establish an absolute pK_a

scale. A two-step procedure was performed. First, the molar extinction coefficient (ϵ) of the anchor anion was determined by titrating a solution of the anchor compound with a solution of a base (1-methylimidazole) at 480 nm. Then, several aliquots of the anchor compound were added into a pure ionic liquid, and the absorbance of the anchor anion was recorded at the same wavelength. The equilibrium concentrations of the parent anchor and its anion can then be calculated from the absorbance and ϵ which then yields the pK_a value. Each pK_a thus derived is the average of the data from six to eight titrations within one run, and the acidity data appeared in Table 1 are the average values of two to three independent runs (reproducible to ≤ 0.05 pK unit).

■ ASSOCIATED CONTENT

● Supporting Information

Table S1, Figures S1–S16, and copies of ^1H NMR and ^{13}C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) King, E. J. *Acid–Base Equilibria*; Pergamon Press: New York, 1965. (b) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, 1973.
- (2) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624.
- (3) For representative examples, see: (a) Breslow, R.; Chu, W. *J. Am. Chem. Soc.* **1973**, *95*, 411. (b) Brauman, J. I. In *Frontiers of Free Radical Chemistry*; Pryor, W. A. Ed.; Academic Press: New York, 1980; pp 23–30. (c) Parker, V. D.; Tilset, M.; Hammerich, O. *J. Am. Chem. Soc.* **1987**, *109*, 7905. (d) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229. (e) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *Science* **1990**, *247*, 423. (f) Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510.
- (4) For representative examples, see: (a) Serjeant, E. P.; Dempsey, B. *Ionisation Constants of Organic Acids in Aqueous Solution*; Pergamon Press: New York, 1979. (b) Stewart, R. *The Proton Application to Organic Chemistry*; Academic Press: New York, 1985.
- (5) (a) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Bordwell, F. G. *Acc. Chem. Soc.* **1988**, *21*, 456 and references cited therein.
- (6) (a) Streitwieser, A.; Hammons, J. H.; Ciuffarin, E.; Brauman, J. I. *J. Am. Chem. Soc.* **1967**, *89*, 59. (b) Bors, D. A.; Kaufman, M. J.; Streitwieser, A. *J. Am. Chem. Soc.* **1985**, *107*, 6975. (c) Streitwieser, A. *J. Org. Chem.* **2009**, *74*, 4433 and references cited therein.
- (7) To name a few, see: (a) Coetzee, J. F.; Kolthoff, I. M. *J. Am. Chem. Soc.* **1957**, *79*, 6110. (b) Arnett, E. M.; Burke, J. J. *J. Am. Chem. Soc.* **1966**, *88*, 2340. (c) Ritchie, C. D.; Megerle, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 1447. (d) Izutsu, K., Eds. *Acid–Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell Scientific Publications: Oxford, 1990. (e) Kütt, A.; Rodima, T.; Saame, J.; Raamat, E.; Mäemets, V.; Kaljurand, I.; Koppel, I. A.; Garlyauskayte, R. Y.; Yagupolskii, Y. L.; Yagupolskii, L. M.; Bernhardt, E.; Willner, H.; Leito, I. *J. Org. Chem.* **2011**, *76*, 391.
- (8) (a) Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. *J. Am. Chem. Soc.* **2003**, *125*, 5264. (b) Malham, I. B.; Letellier, P.; Turmine, M. *Talanta* **2008**, *77*, 48. (c) Angelini, G.; Maria, P. D.; Chiappe, C.; Fontana, A.; Pierini, M.; Siani, G. *J. Org. Chem.* **2010**, *75*, 3912. (d) D'Anna, F.; Marullo, S.; Vitale, P.; Noto, R. *J. Org. Chem.* **2010**, *75*, 4828. (e) Barhdadi, R.; Troupel, M.; Comminges, C.; Laurent, M.; Doherty, A. P. *J. Phys. Chem. B* **2012**, *116*, 277. (f) Johnson, K.; Pagni, R. M.; Bartmess, J. E. *Monatsh. Chem.* **2007**, *138* (11), 1077.
- (9) For representative examples, see: (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772. (c) Wasserscheid, P., Welton, T., Eds. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2008.
- (10) For examples, see: (a) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792. (b) Rantwijk, F. v.; Sheldon, R. A. *Chem. Rev.* **2007**, *107*, 2757. (c) Pinkert, A.; Marsh, K. N.; Pang, S.; Staiger, M. P. *Chem. Rev.* **2009**, *109*, 6712. (d) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621. (e) Rosen, B. A.; Salehi-Khojin, A.; Thorson, M. R.; Zhu, W.; Whipple, D. T.; Kenis, P. J. A.; Masel, R. I. *Science* **2011**, *334*, 643.
- (11) For examples, see: (a) Cheng, J.-P.; Xian, M.; Wang, K.; Zhu, X. Q.; Yin, Z.; Wang, P. G. *J. Am. Chem. Soc.* **1998**, *120*, 10266. (b) Cheng, J.-P.; Liu, B.; Zhao, Y.; Wen, Z.; Sun, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9987. (c) Cheng, J.-P.; Lu, Y.; Zhu, X. Q.; Sun, Y.; Bi, F.; He, J. *J. Org. Chem.* **2000**, *65*, 3853. (d) Zhu, X. Q.; Li, Q.; Hao, W. F.; Cheng, J.-P. *J. Am. Chem. Soc.* **2002**, *124*, 9887. (e) Zhu, X. Q.; Li, H.-R.; Li, Q.; Ai, T.; Lu, J.-Y.; Yang, Y.; Cheng, J.-P. *Chem.—Eur. J.* **2003**, *9*, 871. (f) Chu, Y.; Deng, H.; Cheng, J.-P. *J. Org. Chem.* **2007**, *72*, 7790. (g) Zhu, X. Q.; Zhang, M. T.; Yu, A.; Wang, C. H.; Cheng, J.-P. *J. Am. Chem. Soc.* **2008**, *130*, 2501. (h) Li, X.; Deng, H.; Zhang, B.; Li, J. Y.; Zhang, L.; Luo, S. Z.; Cheng, J.-P. *Chem.—Eur. J.* **2010**, *16*, 450.
- (12) Zhao, W.; Leroy, F.; Heggen, B.; Zahn, S.; Kirchner, B.; Balasubramanian, S.; Müller-Plathe, F. *J. Am. Chem. Soc.* **2009**, *131*, 15825.
- (13) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49.
- (14) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463.
- (15) It should be pointed out that fluorenes show a slightly different acidity order than in $\text{Bm}_2\text{imNTf}_2 > \text{in BmpyNTf}_2 \approx \text{in BmimNTf}_2$ (i.e., the pK_a 's in the latter two ILs are similar) because the greater charge delocalization and the more hindered 9-carbon in fluorenone ions attenuate their solvation with Bmim^+ as compared that with Bmpy^+ .
- (16) The pK_a value of 9-(*p*-bromophenylsulfonyl)-2-(phenylsulfonyl) fluorene was determined in DMSO by the overlapping indicator method.^{5a} For other pK_a values, see ref 5b and: (a) Troughton, E. B.; Molter, K. E.; Arnett, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6726. (b) Koppel, I. A.; Koppel, J.; Pihl, V.; Leito, I.; Mishima, M.; Vlasov, V. M.; Yagupolskii, L. M.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1125.
- (17) (a) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D.-D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047. (b) Bartmess, J. E. *Negative Ion Energetics Data*; Mallard, W. G., Linstrom, P. J., Eds.; NIST Chemistry WebBook, NIST Standard Reference Database No. 69, August 1997, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>).
- (18) Burrell, A. K.; Sesto, R. E. D.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449.
- (19) Bavin, P. M. G. *Can. J. Chem.* **1960**, *38*, 917.

- (20) (a) Uno, M.; Seto, K.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 932. (b) Suzuki, H.; Koide, H.; Ogawa, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 501.
- (21) Ong, B. S.; Chan, T. H. *Synth. Commun.* **1977**, *7*, 283.
- (22) Aleykutty, A. A.; Baliah, V. *J. Indian Chem. Soc.* **1955**, *32*, 702.
- (23) Mahadevan, A.; Fuchs, P. L. *Tetrahedron Lett.* **1994**, *35*, 6025.