Sulfur Oxoacids Hot Paper

DOI: 10.1002/ange.201402577

Straightforward Synthesis of the Brønsted Acid hfipOSO$_3$H and its Application for the Synthesis of Protic Ionic Liquids**

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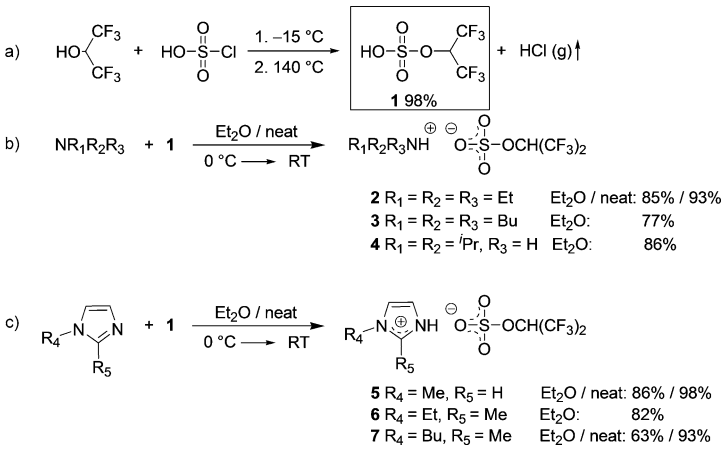
Abstract: *The easily accessible hexafluoroisopropoxysulfuric acid (**1**, hfipOSO$_3$H; hfip = C(H)(CF$_3$)$_2$) was synthesized by the reaction of hexafluoroisopropanol and chlorosulfonic acid on the kilogram scale and isolated in 98 % yield. The calculated gas-phase acidity (GA) value of **1** is 58 kJ mol^{-1} lower in ΔG° than that of sulfuric acid (GA value determined by a CCSD(T)-MP2 compound method). Considering the gas-phase dissociation constant as a measure for the intrinsic molecular acid strength, a hfipOSO$_3$H molecule is more than ten orders of magnitude more acidic than a H$_2$SO$_4$ molecule. The acid is a liquid at room temperature, distillable at reduced pressure, stable for more than one year in a closed vessel, reactive towards common solvents, and decomposes above 180 °C. It is a versatile compound for further applications, such as the synthesis of ammonium- and imidazolium-based air- and moisture-stable protic ionic liquids (pILs). Among the six synthesized ionic compounds, five are pILs with melting points below 100 °C and three of them are liquids at nearly room temperature. The conductivities and viscosities of two representative ILs were investigated in terms of Walden plots, and the pILs were found to be little associated ILs, comparable to conventional aprotic ILs.*

Acidity is one of the main and widely used concepts in chemistry. It plays a key role in basic thermodynamics and is relevant in many fields, such as material science, energy storage, catalysis, environmental science, and molecular biology.[1] According to Brønsted and Lowry, acids are defined as proton donors and bases as proton acceptors.[2] The concept of superacidity has attracted much attention owing to the isolation and characterization of extraordinary compounds, including protonated arenes,[3] protonated fullerenes,[4] carbocations,[5,6] and noble gas compounds.[7] Superacids are commonly defined as acids that are more acidic than neutral sulfuric acid.[8] Very well-known Brønsted superacids are $HClO_4$, HSO_3X (X = Cl, F), R^FSO_3H (R^F = fluorinated organic residue), the binary superacids HF/SbF_5 as well as FSO_3H/SbF_5 ("magic acid"),[5] $(R^FSO_2)_2NH$,[9] $(R^FSO_2)_3CH$,[10] carboranes ($H[HCB_{11}R_5X_6]$; X = Cl, Br, I; R = H, Me, Cl),[4,11] and borane acids $H_2[B_{12}X_{12}]$[12] (X = Cl, Br). The latter two acid types are the strongest isolable superacids known thus far. One well-known concept to increase acidity is the introduction of strongly electron-withdrawing units, including C=NSO$_2$F, C=NSO$_2$CF$_3$, N(CN)$_2$, and C=P(SO$_2$F)$_3$, according to the Yagupolskii principle[13] (also $(R^FSO_2)_2NH$ and $(R^FSO_2)_3CH$). With our experience on weakly coordinating aluminates ($[Al(OR^F)_4]^-$, R^F = fluoroalkyl),[14,15] we decided to substitute a hydrogen atom in sulfuric acid with the hexafluoroisopropyl group (hfip; Scheme 1). Preceding DFT calculations suggested that the hitherto unknown acid hfipOSO$_3$H (**1**) is considerably stronger than sulfuric acid in the gas phase, and that the gas-phase synthesis of **1** according to Scheme 1a should be feasible. Therefore, we pursued the synthesis of this hitherto unexplored system.



Scheme 1. a) Synthesis of the acid **1** and b, c) its application for the preparation of protic ionic liquids **2**–**7**.

To substitute a hydrogen atom in sulfuric acid with the hexafluoroisopropyl group (hfip; Scheme 1). Preceding DFT calculations suggested that the hitherto unknown acid hfipOSO$_3$H (**1**) is considerably stronger than sulfuric acid in the gas phase, and that the gas-phase synthesis of **1** according to Scheme 1a should be feasible. Therefore, we pursued the synthesis of this hitherto unexplored system.

Acid **1** was obtained in bulk quantities by slow addition of hexafluoroisopropanol to chlorosulfonic acid at −15 °C and subsequent stirring at 110 °C until the gas evolution had ceased. Distillation of the product at reduced pressure

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[**] This project was funded by the ERC project UniChem, the DFG, and BASF SE. I.K. and W.B. thank the Fonds der Chemischen Industrie for financial support. hfip = C(H)(CF$_3$)$_2$.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402577.

(10^{-2} mbar) at 60 °C gave the pure acid as a colorless liquid in 98 % yield on a kilogram scale, making it an easily accessible and versatile compound for further syntheses.

The acid **1** was characterized by NMR, IR, and Raman spectroscopy and electrospray ionization (ESI) mass spectrometry, with all signals matching our expectations (Supporting Information, Figure S1). Thus, the acidic proton of the neat compound appears at $\delta(^1H) = 10.42$ ppm as a narrow singlet and the tertiary proton at 5.41 ppm as a septet. The CF_3 groups appear at $\delta(^{19}F) = -75.0$ ppm and can be well distinguished from a hfipOH impurity ($\delta(^{19}F) = -73.0$ ppm); the tertiary C–H signal of an alcohol impurity at $\delta(^1H) =$ 4.68 ppm is often not seen at low concentrations. The IR spectrum shows a very broad band between 3430–2640 cm^{-1}, which is typical for hydrogen bonded systems. The valence C–H stretching mode is visible at 2985 cm^{-1} in the Raman spectrum, whereas it overlaps with the broad O–H vibration in the IR spectrum. The most characteristic band of **1** is the C–H deformation mode at 1362 cm^{-1} (IR) and 1368 cm^{-1} (Raman). The remaining bands could be well assigned to particular modes (see Figure S1 d). In the negative-ion ESI mass spectrum, the main peak was observed at $m/z = 247$ ($[hfipOSO_3]^-$ anion).

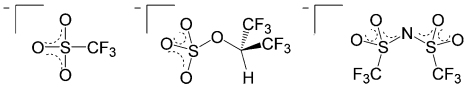
The neat acid **1** is a liquid at ambient temperature and melts just above 0 °C. It appears to be compatible with ether, acetonitrile, dichloromethane, and hexane, but only miscible with the former two solvents. However, protonation NMR experiments, where the solvent was added in small amounts to the acid, revealed that **1** reacts with benzene or toluene (aromatic substitution) and acetonitrile (oligomerization) and forms a protonated species with diethylether [$\delta(^1H) = 11.47$ (acidic proton), 4.57 (q, $^3J(^1H,^1H) = 7.2$ Hz, $O(CH_2CH_3)_2$), 1.65 ppm (t, $^3J(^1H,^1H) = 7.2$ Hz, $O(CH_2CH_3)_2$); $\delta(^{13}C) = 77.1$ ($O(CH_2CH_3)_2$), 12.2 ppm ($O(CH_2CH_3)_2$]. As expected for a very strong acid, it reacts with THF (polymerization) and dimethoxyethane (methyl group cleavage) and even with silicon-based grease. Decomposition of the neat acid occurs above 180 °C. The free acid **1** hydrolyzes in air and in water to give hfipOH and H_2SO_4 and should therefore be kept under anhydrous conditions.

But how acidic is **1**? A well-established measure is the gas-phase acidity (GA), which is defined as the standard Gibbs reaction energy of the dissociation of acid HB (g),

$$HB(g) \xrightleftharpoons{\Delta_r G^\circ = GA} H^+(g) + B^-(g)$$
$$K_a = \exp\left(-\frac{GA}{RT}\right) = \frac{p(H^+)p(B^-)}{p(HB)\,1\,bar} \quad (1)$$

where lower GA values indicate higher acidities. A decrease in the GA value by $RT\ln 10$ (= 5.71 kJ mol^{-1} at 25 °C) increases the dissociation constant by one order of magnitude. High level ab initio quantum chemical calculations with a CCSD(T)-MP2 compound method[16] gave a GA value of 1217 kJ mol^{-1} for **1**, which is thus more acidic than gaseous H_2SO_4 (exp. GA: 1265 ± 10 kJ mol^{-1};[17] calcd. GA: 1272 kJ mol^{-1} [18] and 1274 kJ mol^{-1} (Weizmann-1 level of theory)[16]) by approximately ten orders of magnitude.[19] According to its GA, **1** is more acidic than HSO_3F and HOTf (Tf = SO_2CF_3; calcd. GAs: 1237 kJ mol^{-1} and 1226 kJ mol^{-1})[18] but still somewhat less acidic than $HNTf_2$ (exp. GA: 1199 kJ mol^{-1}; calcd. GA: 1196 kJ mol^{-1}).[20]

Therefore, the conjugate base of **1**, the anion $[hfipOSO_3]^-$ (**III**) appeared to be a suitable constituent of ionic liquids (ILs). Its relation to $[OTf]^-$ (**I**) and $[NTf_2]^-$ (**II**), both common constituents of ILs, is shown in Scheme 2. The $[hfipOSO_3]^-$ anion can be seen as an extended $[OTf]^-$ anion, where the CF_3 residue is substituted by a hfipO group. The close similarity of anions **II** and **III** can be described in the following way:



	I	III	II
V_m / nm^3	0.126	0.204[a]	0.230[a]
S / nm^2	1.277	1.800[a]	2.035[a]

Scheme 2. The $[hfipOSO_3]^-$ anion (**III**) and its analogues $[OTf]^-$ (**I**) and $[NTf_2]^-$ (**II**) along with their scaled molecular volumes and surfaces. The latter quantities were calculated as described elsewhere.[23,24]
[a] Low-energy conformer.

Conformational freedom and symmetry are the main factors influencing the melting entropy ($\Delta_m S$) and consequently the melting point (T_m).[21] The existence of several conformational degrees of freedom hinders efficient packing, thus leading to a decrease in T_m. The occurrence of higher symmetry increases the number of possible equivalent positions in the crystal, and thus the solid-state entropy. Consequently, $\Delta_m S$ is reduced, which would lead to a higher T_m.[21] These two counterbalancing effects occur in **II** and **III**. The $[NTf_2]^-$ anion can adopt two conformations separated by only a few kJ mol^{-1} in the gas, liquid, and solid phase.[22] The lowest-energy conformer in the gas phase has C_2 symmetry. We found two minimum conformations for the $[hfipOSO_3]^-$ anion, which are separated by 49 (37) kJ mol^{-1} at the PBE0/def-TZVPP (BP86/def2-TZVP) level of theory, so that the higher-energy conformer can be neglected in thermodynamic considerations. The global-energy-minimum conformer of **III** is of lower symmetry (idealized C_s symmetry) than **II**. The similarities of **II** and **III** are corroborated by their molecular volumes and surfaces (Scheme 2), which are the key quantities determining the melting enthalpy and thus T_m of ILs.[21] Therefore, with regard to melting enthalpy and entropy, ILs with **II** and **III** as the anion should have comparable T_m values and, because of the high acidities of the parent acids and the delocalized nature of the charges, similar and very favorable IL forming qualities.

These considerations could be verified by the synthesis of protic ILs (pILs; Scheme 1) by the addition of an imidazole or amine base to **1** at 0 °C, either with or without solvent. Good to high yields were obtained in diethyl ether (63–86 %) or, preferably, without solvent (93–98 %). The phase-transition properties of compounds **2**–**7** are summarized in Table 1. Five of the compounds are ILs, with four of them being nearly room temperature (RT) ILs. The similarities between **I**, **II**, and **III** are also confirmed by the rather low melting points of $[C_1HIM][hfipOSO_3]$ (**5**; 34 °C) and the related compounds $[C_2C_1HIM][OTf]$ (33 °C[25]) and $[C_1HIM][NTf_2]$ (52 °C)

Table 1: Phase-transition properties of compounds **2**–**7**.[a]

Compound	T_m [°C]	T_c [°C]	$T_{s\text{-}s}$ [°C]	T_{cc} [°C]	T_g [°C]
$[HNEt_3][hfipOSO_3]$ (**2**)	42	na[b]	38[c]		
$[HNBu_3][hfipOSO_3]$ (**3**)	81	58	−55		
$[H_2NiPr_2][hfipOSO_3]$ (**4**)	145	139	7, −39		
$[C_1HIM][hfipOSO_3]$ (**5**)	34	na[d]			
$[C_2C_1HIM][hfipOSO_3]$ (**6**)	33	−3[e]		−15[f]	−53[g]
$[C_4C_1HIM][hfipOSO_3]$ (**7**)	31			−5	−52

[a] If not otherwise noted, these temperatures were identified as extrapolated onset temperatures of the differential scanning calorimetry (DSC) curves. [b] Not assigned because of non-uniform and non-reproducible crystallization between 20 °C and −20 °C. [c] Peak temperature, as this phase transition overlaps with the melting process, and the onset can only be assigned to the main peak. [d] Not assigned because of unreproducible crystallization behavior between 4 and 7 °C. [e] Partial crystallization during cooling. [f] Peak temperature, since consistent values in two subsequent runs were obtained. [g] Heating rate: 20 K min^{-1}; glass transition did not occur at a heating rate of 5 K min^{-1}. T_g: glass transition temperature, T_m: melting temperature, T_c: crystallization temperature, $T_{s\text{-}s}$: solid–solid phase-transition temperature during heating, T_{cc}: cold crystallization temperature.

($[C_1HIM]^+ = N$-methylimidazolium, $[C_2C_1HIM]^+ = N$-ethyl-2-methylimidazolium).[26,27] With the exception of **3**, these compounds did not hydrolyze when kept in air for several days or when dissolved in pure D_2O. These findings facilitate the handling of the synthesized pILs and their use for further applications.

Compounds **2**, **6**, and **7** were successfully crystallized, and the crystal structure of **7** is shown exemplarily in Figure 1. The bond lengths in **2**, **6**, and **7** correspond to the tabulated average bond lengths of organic compounds[28] and are

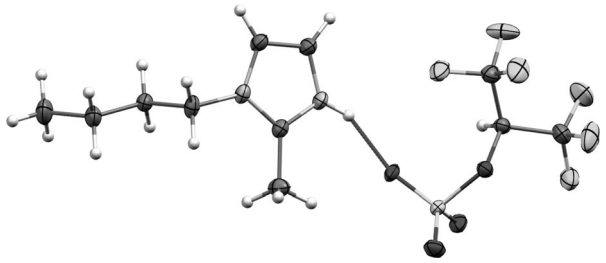


Figure 1. Asymmetric unit of the crystal structure of **7**. Thermal ellipsoids set at 50% probability. The line between the cation and anion shows the N–H···O hydrogen bond. The S–O distances (in Å) are as follows: $d_{S1\text{–}O1} = 1.4289(11)$, $d_{S1\text{–}O2} = 1.4366(11)$, $d_{S1\text{–}O3} = 1.4479(9)$, $d_{S1\text{-}O4} = 1.6578(8)$.

therefore not further discussed. The torsion angle S1-O4-C1-H1 is close to 0° in all structures; this is also the global minimum according to the quantum chemical calculations. Intermolecular N–H···O hydrogen bonds ($d_{H\cdots O} = 1.89(3)$–$1.954(18)$ Å, $d_{N\cdots O} = 2.577(2)$–$2.801(3)$ Å) and various short C–H···O contacts ($d_{H\cdots O} = 2.23$–2.58 Å, $d_{C\cdots O} = 2.800(5)$–$3.526(5)$ Å) exist in compounds **2**, **6**, and **7**.

Temperature-dependent viscosities (η) and conductivities (κ) of one representative ammonium (**2**) and an imidazolium (**7**) salt were measured. The viscosity (conductivity) at 40 °C (50–51 °C) of **2** (47 mPa s and 4.15 mS·cm^{-1}) is lower (higher) than that of **7** (110 mPa s and 2.10 mS·cm^{-1}). Only few studies on pILs with the triethylammonium cation exist,[29] and therefore, we concentrate on the properties of **7** for further discussions. At 40 °C, compound **7** has a viscosity that is comparable to that of related alkylimidazolium $[NTf_2]^-$ pILs (54–100 mPa s at 25 °C), but is usually less viscous than the corresponding $[ClO_4]^-$, $[PF_6]^-$, $[OTf]^-$, and $[N(SO_2C_2F_5)_2]^-$ pILs.[25] The conductivity of **7** at 50 °C is below the conductivities for related alkylimidazolium $[NTf_2]$ pILs (ca. 6–18 mS·cm^{-1}), but significantly exceeds the conductivity of ethylimidazolium halides (ca. 0.3–0.03 mS·cm^{-1}).[25] The Walden plots of **2** and **7** show that these ILs can be classified as "good ILs",[30] that is, less associated ILs (Figure 2).

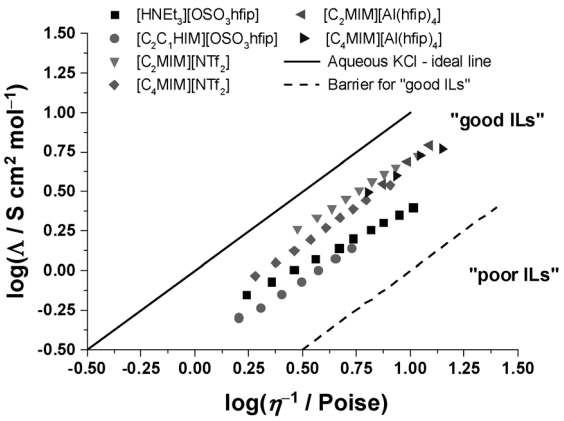


Figure 2. Walden plot of the ILs **2** and **7** along with Walden plots for typical organic salts. The data for the $[NTf_2]^-$ and $[Al(Ohfip)_4]^-$ based ILs were taken from Refs. [15, 31]: η = viscosity, Λ = molar conductivity, obtained as the ratio of the electrical conductivity (κ) and the density (ρ). The latter was calculated as described by Preiss et al.[23]

This is in contrast to other pILs, which are usually considered to be "poor ILs".[29] Furthermore, the Walden plot shows that the investigated salts **2** and **7** are even comparable to conventional $[NTf_2]^-$ and $[Al(Ohfip)_4]^-$ based aprotic ILs.[15,31] With regard to the low melting points of these ILs, the syntheses of the corresponding aprotic ILs and an investigation of their transport properties should be highly promising.

In summary, we have presented a highly efficient synthesis and a thorough characterization of the novel and easily accessible Brønsted acid $hfipOSO_3H$, which might be used as a basis for new superacidic systems or even might be a superacid itself. Investigations in this direction are ongoing. Furthermore, it was shown that the $[hfipOSO_3]^-$ anion is a suitable constituent for the formation of low-melting-point ILs. In future work, the synthesis and properties of aprotic ILs with the $[hfipOSO_3]^-$ anion and its inorganic salts and their potential as Li electrolytes will be investigated.

Received: February 20, 2014
Published online: May 26, 2014

Keywords: Brønsted acids · gas-phase acidity · ionic liquids · quantum chemistry

[1] a) R. B. Bell, *The Proton in Chemistry*, 2nd ed., Chapman and Hall, London, **1973**; b) J. P. Sohn, *Trends Chem. Eng.* **2003**, *8*, 105; c) R. Devanathan, *Energy Environ. Sci.* **2008**, *1*, 101; d) H. Yamamoto, K. Ishihara, *Acid Catalysis in Modern Organic Synthesis*, Wiley-VCH, Weinheim, **2008**; e) K. Arata *in Metal Oxide Catalysis* (Eds.: S. D. Jackson, J. S. J. Hargreaves), Wiley-VCH, Weinheim, **2009**; f) R. J. Charlson, H. Rodhe, *Nature* **1982**, *295*, 683; g) B. P. Pedersen, M. J. Buch-Pedersen, J. P. Morth, M. G. Palmgren, P. Nissen, *Nature* **2007**, *450*, 1111.

[2] a) J. N. Brönsted, *Recl. Trav. Chim. Pays-Bas* **1923**, *42*, 718; b) T. M. Lowry, *Chem. Ind.* **1923**, *42*, 43.

[3] C. A. Reed, K.-C. Kim, E. S. Stoyanov, D. Stasko, F. S. Tham, L. J. Mueller, P. D. W. Boyd, *J. Am. Chem. Soc.* **2003**, *125*, 1796.

[4] C. A. Reed, K.-C. Kim, R. D. Bolskar, L. J. Mueller, *Science* **2000**, *289*, 101.

[5] G. A. Olah, G. K. S. Prakash, Á. Molnár, J. Sommer, *Superacid Chemistry*, 2nd ed., Wiley, Hoboken, **2009**.

[6] F. Scholz, D. Himmel, H. Scherer, I. Krossing, *Chem. Eur. J.* **2013**, *19*, 109.

[7] a) T. Drews, K. Seppelt, *Angew. Chem.* **1997**, *109*, 264; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 273; b) S. Seidel, K. Seppelt, *Science* **2000**, *290*, 117; c) T. Drews, S. Seidel, K. Seppelt, *Angew. Chem.* **2002**, *114*, 470; *Angew. Chem. Int. Ed.* **2002**, *41*, 454.

[8] R. J. Gillespie, T. E. Peel, E. A. Robinson, *J. Am. Chem. Soc.* **1971**, *93*, 5083.

[9] J. Foropoulos, D. D. DesMarteau, *Inorg. Chem.* **1984**, *23*, 3720.

[10] L. Turowsky, K. Seppelt, *Inorg. Chem.* **1988**, *27*, 2135.

[11] a) D. Stasko, C. A. Reed, *J. Am. Chem. Soc.* **2002**, *124*, 1148; b) C. A. Reed, *Chem. Commun.* **2005**, 1669; c) E. S. Stoyanov, S. P. Hoffmann, M. Juhasz, C. A. Reed, *J. Am. Chem. Soc.* **2006**, *128*, 3160; d) M. Juhasz, S. Hoffmann, E. Stoyanov, K.-C. Kim, C. A. Reed, *Angew. Chem.* **2004**, *116*, 5466; *Angew. Chem. Int. Ed.* **2004**, *43*, 5352; e) E. S. Stoyanov, K.-C. Kim, C. A. Reed, *J. Am. Chem. Soc.* **2006**, *128*, 8500.

[12] a) A. Avelar, F. S. Tham, C. A. Reed, *Angew. Chem.* **2009**, *121*, 3543; *Angew. Chem. Int. Ed.* **2009**, *48*, 3491; b) R. T. Boeré, S. Kacprzak, M. Keßler, C. Knapp, R. Riebau, S. Riedel, T. L. Roemmele, M. Rühle, H. Scherer, S. Weber, *Angew. Chem.* **2011**, *123*, 572; *Angew. Chem. Int. Ed.* **2011**, *50*, 549.

[13] a) N. V. Kondratenko, V. I. Popov, O. A. Radchenko, N. V. Ignatev, L. M. Yagupolskii, *Zh. Org. Khim.* **1986**, *22*, 1716; b) L. M. Yagupolskii, V. I. Popov, N. V. Pavlenko, I. I. Maletina, A. A. Mironova, R. Y. Gavrilova, V. V. Orda, *Zh. Org. Khim.* **1986**, *22*, 2169; c) L. M. Yagupolskii, *Aromatic and Heterocyclic Compounds with Fluorine-Containing Substituents*, Naukova Dumka, Kiev, **1988**; d) I. A. Koppel, P. Burk, I. Koppel, I. Leito, *J. Am. Chem. Soc.* **2002**, *124*, 5594.

[14] a) I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490; b) I. Krossing, I. Raabe, *Angew. Chem.* **2004**, *116*, 2116; *Angew. Chem. Int. Ed.* **2004**, *43*, 2066; c) I. Krossing, A. Reisinger, *Coord. Chem. Rev.* **2006**, *250*, 2721; d) I. Raabe, K. Wagner, K. Guttsche, M. Wang, M. Grätzel, G. Santiso-Quiñones, I. Krossing, *Chem. Eur. J.* **2009**, *15*, 1966.

[15] S. Bulut, P. Klose, M. M. Huang, H. Weingärtner, P. J. Dyson, G. Laurenczy, C. Friedrich, J. Menz, K. Kummerer, I. Krossing, *Chem. Eur. J.* **2010**, *16*, 13139.

[16] See the Supporting Information for the quantum chemical calculations.

[17] A. A. Viggiano, M. J. Henchman, F. Dale, C. A. Deakyne, J. F. Paulson, *J. Am. Chem. Soc.* **1992**, *114*, 4299.

[18] K. E. Gutowski, D. A. Dixon, *J. Phys. Chem. A* **2006**, *110*, 12044.

[19] In analogy to the liquid-phase process, where the dissociation constants and the proton activities show the same exponential relationship, one can say that the intrinsic acid strength in the gas phase increases by one order of magnitude when $\Delta GA = -5.71\ kJ\,mol^{-1}$.

[20] I. Leito, E. Raamat, A. Kütt, J. Saame, K. Kipper, I. A. Koppel, I. Koppel, M. Zhang, M. Mishima, L. M. Yagupolskii, R. Y. Garlyauskayte, A. A. Filatov, *J. Phys. Chem. A* **2009**, *113*, 8421.

[21] U. P. Preiss, W. Beichel, A. M. T. Erle, Y. U. Paulechka, I. Krossing, *ChemPhysChem* **2011**, *12*, 2959.

[22] a) K. Fujii, T. Fujimori, T. Takamuku, R. Kanzaki, Y. Umebayashi, S. I. Ishiguro, *J. Phys. Chem. B* **2006**, *110*, 8179; b) J. C. Lassègues, J. Grondin, R. Holomb, P. Johansson, *J. Raman Spectrosc.* **2007**, *38*, 551; c) M. Herstedt, W. A. Henderson, M. Smirnov, L. Ducasse, L. Servant, D. Talaga, J. C. Lassègues, *J. Mol. Struct.* **2006**, *783*, 145; d) Y. Umebayashi, T. Mitsugi, K. Fujii, S. Seki, K. Chiba, H. Yamamoto, J. N. Canongia Lopes, A. A. H. Pádua, M. Takeuchi, R. Kanzaki, S.-i. Ishiguro, *J. Phys. Chem. B* **2009**, *113*, 4338; e) A. Martinelli, A. Matic, P. Johansson, P. Jacobsson, L. Börjesson, A. Fernicola, S. Panero, B. Scrosati, H. Ohno, *J. Raman Spectrosc.* **2011**, *42*, 522.

[23] U. P. R. M. Preiss, J. M. Slattery, I. Krossing, *Ind. Eng. Chem. Res.* **2009**, *48*, 2290.

[24] W. Beichel, U. P. Preiss, S. P. Verevkin, T. Koslowski, I. Krossing, *J. Mol. Liq.* **2014**, *192*, 3.

[25] H. Ohno, M. Yoshizawa, *Solid State Ionics* **2002**, *154–155*, 303.

[26] a) T. Peppel, C. Roth, K. Fumino, D. Paschek, M. Köckerling, R. Ludwig, *Angew. Chem.* **2011**, *123*, 6791; *Angew. Chem. Int. Ed.* **2011**, *50*, 6661; b) A. M. Moschovi, S. Ntais, V. Dracopoulos, V. Nikolakis, *Vib. Spectrosc.* **2012**, *63*, 350.

[27] Ohno et al. report a melting point of 9 °C; see Ref. [25]. At the same time, the authors cite the water content of this IL as < 5000 ppm. Such a water content is rather high and may lead to a large melting-point depression and surely also has an influence on the physical properties. Because of a lack of additional data, the viscosity and conductivity data for this compound were taken from Ref. [25] for comparisons with our results.

[28] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[29] T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206.

[30] a) W. Xu, E. I. Cooper, C. A. Angell, *J. Phys. Chem. B* **2003**, *107*, 6170; b) M. Yoshizawa, W. Xu, C. A. Angell, *J. Am. Chem. Soc.* **2003**, *125*, 15411.

[31] S. Bulut, P. Eiden, W. Beichel, J. M. Slattery, T. F. Beyersdorff, T. J. S. Schubert, I. Krossing, *ChemPhysChem* **2011**, *12*, 2296.

