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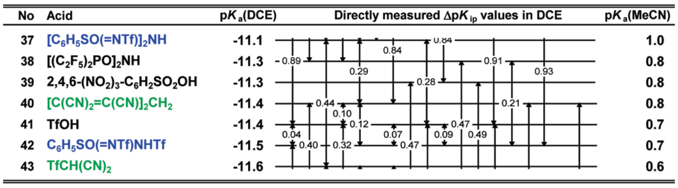
# Equilibrium Acidities of Superacids

Agnes Kütt,* Toomas Rodima, Jaan Saame, Elin Raamat, Vahur Mäemets,
Ivari Kaljurand, Ilmar A. Koppel,* Romute Yu. Garlyauskayte, Yurii L. Yagupolskii,
Lev M. Yagupolskii, Eduard Bernhardt, Helge Willner, and Ivo Leito*

*Institute of Chemistry, University of Tartu, Ravila 14a, Tartu, 50411, Estonia, Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya 5, Kiev, 02094, Ukraine, and Anorganische Chemie, Bergische Universität Wuppertal, Gaussstrasse 20, D-42097 Wuppertal, Germany*

*agnes.kutt@ut.ee; ilmar.koppel@ut.ee; ivo.leito@ut.ee*

*Received July 25, 2010*



| No | Acid | p$K_a$(DCE) | Directly measured Δp$K_{ip}$ values in DCE | p$K_a$(MeCN) |
|---|---|---|---|---|
| 37 | [$C_6H_5SO(=NTf)]_2NH$ | -11.1 | | 1.0 |
| 38 | $[(C_2F_5)_2PO]_2NH$ | -11.3 | | 0.8 |
| 39 | 2,4,6-$(NO_2)_3$-$C_6H_2SO_2OH$ | -11.3 | | 0.8 |
| 40 | $[C(CN)_2=C(CN)]_2CH_2$ | -11.4 | | 0.8 |
| 41 | TfOH | -11.4 | | 0.7 |
| 42 | $C_6H_5SO(=NTf)NHTf$ | -11.5 | | 0.7 |
| 43 | $TfCH(CN)_2$ | -11.6 | | 0.6 |

In this paper, we report the most comprehensive equilibrium superacidity scale that is available to date. Contrary to most of the past works, this scale is set up in a medium of constant composition and the obtained acidity values characterize the acidities of molecules rather than acidities of media. The current scale is thus complementary to the well-known $H_0$ scale in the information that it provides. The solvent used is 1,2-dichloroethane (DCE). DCE has very weak basic properties (but sufficiently high polarity) and is an appropriate solvent for measuring acidities of very strong acids of diverse chemical nature. DCE acidities of well-known superacids ($CF_3SO_2OH$, $(CF_3SO_2)_2NH$, cyanocarbon acids, etc.) as well as common mineral acids ($H_2SO_4$, HI, HBr, etc.) are reported. Acidities of altogether 62 acids have been determined from 176 interlinked relative acidity measurements. The scale spans 15 orders of magnitude (from picric acid to 1,1,2,3,3-pentacyanopropene) and is expected to be a useful tool in design, use, and further acidity measurements of superacidic molecules.

## Introduction

Acids of very high strength—superacids[1]—and their anions (often behaving as weakly coordinating anions—WCAs) have found a wide area of applications.[2–5] WCAs are of key importance as counterions in catalysis and the stabilizing of highly reactive species, as well as charge carriers in electrochemical power sources.[6–10]

Cyanocarbon acids,[11–13] sulfonic acids,[3] sulfonimides,[5,14] and other types of strong acids have been known and used for a long time, but equilibrium acidity data in solution on most of these acids range from scarce to at best inconsistent[15] and often rely on indirect methods.[16] Although (besides their

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*To whom correspondence should be addressed at the University of Tartu.

[1] The term "superacid" refers in this paper to a superacidic compound not to a superacidic medium. A superacidic compound can be defined as a compound having in a particular medium, e.g., gas phase or some solvent, higher acidity than $H_2SO_4$.

[2] (a) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Science* **1979**, *206*, 13–20. (b) Olah, G. A.; Prakash, G. K. S.; Molnár, A.; Sommer, J. *Superacid Chemistry*; Wiley-Interscience: New York, 2009.

[3] Harmer, M. A.; Junk, C.; Rostovtsev, V.; Carcani, L. G.; Vickery, J.; Schnepp, Z. *Green Chem.* **2007**, *9*, 30–37.

[4] Hasegawa, A.; Naganawa, Y.; Fushimi, M.; Ishihara, K.; Yamamoto, H. *Org. Lett.* **2006**, *8*, 3175–3178.

[5] Posternak, G.; Garlyauskayte, R. Yu.; Yagupolskii, L. M. *Tetrahedron Lett.* **2009**, *50*, 446–447.

[6] Reed, C. A.; Kim, K.-C.; Bolskar, R. D.; Mueller, L. J. *Science* **2000**, *289*, 101–104.

[7] DesMarteau, D. D. *Science* **2000**, *289*, 72–73.

[8] Reed, C. *Acc. Chem. Res.* **1998**, *31*, 133–139.

[9] Krossing, I.; Raabe, I. *Chem.—Eur. J.* **2004**, *10*, 5017–5030.

[10] Küppers, T.; Bernhardt, E.; Eujen, R.; Willner, H.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 6346–6349.

[11] Middleton, W. J.; Little, E. L.; Coffman, D. D.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1958**, *80*, 2795–2806.

[12] Boyd, R. H. *J. Phys. Chem.* **1963**, *67*, 737–744.

[13] Rappoport, Z. *The Chemistry of the Cyano Group*; Interscience: London, UK, 1970.

[14] (a) Garlyauskayte, R. Y.; Chernega, A. N.; Michot, C.; Armand, M.; Yagupolskii, Y. L.; Yagupolskii, L. M. *Org. Biomol. Chem.* **2005**, *3*, 2239–2243. (b) Posternak, A. G.; Garlyauskayte, R. Y.; Polovinko, V. V.; Yagupolskii, L. M.; Yagupolskii, Y. L. *Org. Biomol. Chem.* **2009**, *7*, 1642–1645.

[15] Webster, W. *J. Am. Chem. Soc.* **1966**, *88*, 3046–3050.

[16] Stoyanov, I. E.; Kim, K.-C.; Reed, C. *J. Am. Chem. Soc.* **2006**, *128*, 8500–8508.

DOI: 10.1021/jo101409p Published on Web 12/17/2010
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gas-phase acidities[17,18]) the $pK_a$ values of some of them have been published in acetic acid,[19] most of the acidity data have been obtained in solvent mixtures of varying composition, such as aqueous $H_2SO_4$ at different concentrations[2] or acetonitrile acidified to different extents,[15] i.e. not in constant-composition liquid media. The reported infrared spectroscopic scale of the ion-pairing ability of superacid anions with trioctylammonium counterions—the $\nu$NH scale[16]—is useful for characterizing anions of superacids, but is not an equilibrium acidity scale and characterizes the hydrogen bond acceptor strength of anions rather than the Brønsted acidity of their parent acids.

The choice of the medium for measurements of the acid strength of strong acids is not simple. Typical solvents are either not convenient for acid−base measurements because of low polarity, poor solvating ability of ions, and polar solutes (e.g., heptane,[20] $SO_2$) or are too basic (e.g., DMSO,[21] MeCN[22]) for studying strong acids.

In this work, the equilibrium acidities of a large range of strong acids, many of them superacids, have been measured in 1,2-dichloroethane (DCE) and we present the most comprehensive equilibrium superacidity scale that is available to date in a medium of constant composition.

DCE is an appropriate solvent for studying superacids because it combines negligible basic properties and inertness with the ability to dissolve many polar and ionic compounds. Although its relative permittivity ($\varepsilon_r = 10.60$) is among the highest known for chloroalkanes, it is still too low to efficiently support the dissociation of ion pairs into free ions.[23] For this reason and because of its low ion-solvating ability, relative ion-pair acidities ($\Delta pK_{ip}$) are directly measured. The low polarity also causes several side processes in acidity measurements: ion-pair formation and homoconjugation are more extensive in DCE than, for example, in MeCN.

The $pK_a$ value is used to describe the equilibrium acidity of an acid HA in a solvent S:

$$\mathrm{HA} + \mathrm{S} \overset{K_a}{\rightleftarrows} \mathrm{A}^- + \mathrm{SH}^+ \tag{1}$$

$$pK_a = -\log \frac{a(\mathrm{SH}^+)\cdot a(\mathrm{A}^-)}{a(\mathrm{HA})} \tag{2}$$

Using the approach[22,24] based on relative acidity measurements of acids $HA_1$ and $HA_2$ (see the SI for a description of the measurement method) there is no need to determine the activity of the solvated proton in the medium, $a(\mathrm{HS}^+)$, or to take into account the formation of ion pairs of the acid anion and protonated base ($\mathrm{HB^+A_1^-}$ and $\mathrm{HB^+A_2^-}$) during the relative direct acidity measurements:

$$\mathrm{HA_1} + \mathrm{HB^+A_2^-} \overset{\Delta K_{ip}}{\rightleftarrows} \mathrm{HA_2} + \mathrm{HB^+A_1^-} \tag{3}$$

$$\Delta pK_{ip} = \log \frac{a(\mathrm{HB^+A_1^-})\cdot a(\mathrm{HA_2})}{a(\mathrm{HB^+A_2^-})\cdot a(\mathrm{HA_1})} \tag{4}$$

Assuming that the ratio of activity coefficients of the ion-paired and neutral species of both acids are similar at any acidity of the solution—$f(\mathrm{HB^+A_1^-})/f(\mathrm{HA_1}) = f(\mathrm{HB^+A_2^-})/f(\mathrm{HA_2})$—concentrations of the species can be used instead of their activities. The counterion $\mathrm{HB^+}$ of the acid anions is the protonated phosphazene base $t$-Bu$P_1$(pyrr) (in a few cases $\mathrm{Alk_4N^+}$). It is important to emphasize that the directly measured acidities are so-called ion-pair acidities. Nevertheless, their *differences* are expected to reflect the differences of the free ion acidities of the acids: $\Delta pK_a \approx \Delta pK_{ip}$

$$pK_a(\mathrm{HA_2}) - pK_a(\mathrm{HA_1}) = \Delta pK_a \approx \Delta pK_{ip} = \log \frac{[\mathrm{HB^+A_1^-}]\cdot[\mathrm{HA_2}]}{[\mathrm{HB^+A_2^-}]\cdot[\mathrm{HA_1}]} \tag{5}$$

The necessary condition for this is that the ion-pairing affects both anions in a similar way and, in particular, there must be no hydrogen bonding involved. Some of the smaller anions (such as $\mathrm{Cl^-}$ and $\mathrm{BF_4^-}$) may be more strongly influenced by ion pairing and this may lead to a shift of their $pK_a$ values in the scale relative to the acids with larger anions. Nevertheless, this is not expected to influence the span of the scale itself because its backbone is built by using acids that on deprotonation give anions with efficiently delocalized charge. Such acids and their anions are also not significantly influenced by traces of water in the solvent.[25] Since correcting for this ion-pairing would be somewhat artificial and introduce additional assumptions (see ref 26) we decided not to correct and leave the data as they are.

The formation of hydrogen bonding between the acid anions and the protonated base is hindered by the choice of the base—$t$-Bu$P_1$(pyrr). The proton in protonated $t$-Bu$P_1$-(pyrr) is buried between the bulky substituents and the charge of the bulky cation is highly delocalized. There is strong evidence against hydrogen bonding between the acid anions and the protonated phosphazene base:

(1) Low hydrogen bond donicity of protonated phosphazenes was among the goals for which phosphazene bases were initially developed by the Schwesinger group.[27] The proton in the protonated forms of the bulky phosphazene bases is buried between substituents. This is especially true if the substituent on the imino nitrogen is bulky ($t$-Bu in our case) and if the substituents on the phosphorus are large, such as pyrrolidinyl (our case), tetramethyl guanidinyl, etc. The hindrance of the proton in protonated phosphazenes has

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[17] Koppel, A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignatev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047–3057.

[18] Leito, I.; Raamat, E.; Kütt, A.; Saame, J.; Kipper, K.; Koppel, I. A.; Koppel, I.; Zhang, M.; Mishima, M.; Yagupolskii, L. M.; Garlyauskayte, R. Y.; Filatov, A. A. *J. Phys. Chem. A* **2009**, *113*, 8421–8424.

[19] (a) Engelbrecht, A.; Rode, B. M. *Monatsh. Chem.* **1972**, *103*, 1315–1319. (b) Foropoulos, J.; Desmarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720–3723.

[20] Rõõm, E.-I.; Kaljurand, I.; Leito, I.; Rodima, T.; Koppel, I. A.; Vlasov, V. M. *J. Org. Chem.* **2003**, *68*, 7795–7799.

[21] Bordwell, G. *Acc. Chem. Res.* **1988**, *21*, 456–463.

[22] Kütt, A.; Leito, I.; Kaljurand, I.; Sooväli, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. *J. Org. Chem.* **2006**, *71*, 2829–2838.

[23] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, Germany, 2003.

[24] Leito, I.; Rodima, T.; Koppel, I. A.; Schwesinger, R.; Vlasov, V. M. *J. Org. Chem.* **1997**, *62*, 8479–8483.

[25] Kaupmees, K.; Kaljurand, I.; Leito, I. *J. Phys. Chem. A* **2010**, *114*, 11788–11793.

[26] Kaljurand, I.; Rodima, T.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A.; Mishima, M. *J. Org. Chem.* **2003**, *68*, 9988–9993.

[27] Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H. W.; Bordwell, F. G.; Satish, A. V.; Ji, G.-Z.; Peters, E.-M.; Peters, K.; Schnering, H. G. V.; Walz, L. *Liebigs Ann.* **1996**, 1055.

[28] Kolomeitsev, A. A.; Koppel, I. A.; Rodima, T.; Barten, J.; Lork, E.; Röschenthaler, G.-V.; Kaljurand, I.; Kütt, A.; Koppel, I.; Mäemets, V.; Leito, I. *J. Am. Chem. Soc.* **2005**, *127*, 17656–17666.

been demonstrated by X-ray diffractograms.[27,28] A particularly noteworthy feature of phosphazenium cations in the context of this paper is their ready applicability in the preparation of the so-called "naked fluorides".[29] Cations behaving as inert toward the highly HB-acceptory fluoride anion can be safely considered the same with respect to all anions of this study.

(2) The absence of hydrogen bond between the protonated phosphazene base and acid anions is also seen from the UV−vis spectra that are recorded during the measurement. When phosphazene base *t*-BuP$_1$(pyrr) is used as titrant no distortion of the spectra of acid−anion mixtures is observed. At the same time, titration of some of the acids (**1**, **13**, **17**, **21**, **24**, **28**, and **29**) with triethylamine (or being originally triethylammonium or pyridinium salts) caused distortion of the spectral plot (a hypsochromic shift of the maximum of spectrum) and strongly inconsistent results. This is a clear indication of formation of a hydrogen-bonded complex. The same effect was never experienced with *t*-BuP$_1$(pyrr). For double-checking, some of the compounds were also titrated with an even bulkier base *t*-BuP$_4$(dma) and the spectra matched with the spectra obtained from the titration with base *t*-BuP$_1$(pyrr). The *t*-BuP$_1$(pyrr) base was preferred because it is a sufficiently strong base[30] and is commercially available with reasonable purity and price.

Thus, we might have relatively loosely bound ion pairs between a sterically hindered huge cation (with diameter over 9 Å) and different anions of (mostly) CH acids with well delocalized negative charge, but not hydrogen-bonded complexes.

## Results

The results of acidity measurements are presented in Table 1. p$K_a$ values of 62 acids are interconnected with 176 relative acidity measurements to obtain a self-consistent acidity scale ranging in total for 15 p$K_{ip}$ units. The exact positions of individual acids on the scale were found as in previous works[22,24] by minimizing the sum of squares of differences between the measured $\Delta$p$K_{ip}$ values and the differences of the assigned p$K_a$ values. The agreement between the overlapping measurements (i.e., the $\Delta$p$K_{ip}$ of A vs B plus $\Delta$p$K_{ip}$ of B vs C must be equal to $\Delta$p$K_{ip}$ of A vs C) is very good as indicated by the consistency standard deviation of the scale 0.032 units.[22,24]

Our method allows for the measurement of relative acidities expressed as $\Delta$p$K_{ip}$ values. To obtain absolute p$K_a$ values, the scale has to be anchored to an acid with a known p$K_a$ value. There are currently no reliable absolute experimental p$K_a$ values available in DCE (see discussion in the SI[31]). We thus keep the scale relative at this time, and anchor the scale to the p$K_a$ value of picric acid 1, which is arbitrarily assigned to 0.0 units.

## Discussion

The set of 62 acids directly measured to the present scale (plus acids **63** and **64** with estimated acidities) includes all common strong mineral acids and a number of superacids from different families. The critical factor for the acidity of a superacid is the stability of its anion and the lack of well-defined protonation centers in the anion.[7] It is fair to say that designing a superacid depends largely on the design of the corresponding anion.[32]

From Table 1 two different design concepts of superacid anions emerge as the most potent in enhancing acidity:[33] cyanocarbon anions[34] (denoted with green color) and anions of poly-SO$_2$X-imides and methanes (blue color). Both of these anion groups obtain their stability from the excellent charge delocalization but with different mechanisms. Cyanocarbon anions are a beautiful example of delocalization of the negative charge by efficient polar resonance in a planar (or nearly planar) C$_3$ (**45**, **49**, **52**, **54**, **62**, etc.) or C$_5$ (**19**, **61**) moiety.[35,36] In the sulfo-anions the efficient combination of a polarizable sulfur atom with the high electron-acceptor power of the $=$O atoms (or the even much higher electron-acceptor power of the $=$N-Tf[37] fragments) is engaged. Both of these concepts lead to the formation of anions that have a number of protonation centers with similar (and very low) basicity.

Of the acids not belonging to either of these groups the strongest is HB(CN)$_4$ **58**. Although composed according to a different principle, its anion displays charge delocalization similar to anions of the cyanocarbon acids by forming 4 equally weakly basic protonation centers. Anion B(CN)(CF$_3$)$_3^-$ **31** is a good example of the loss of this symmetry: the CF$_3$ groups with their weaker electron-acceptor power leave the single −CN significantly more basic than in B(CN)$_4^-$ and as a result **31** is by 4 orders of magnitude weaker acid than **58**. HB(CN)$_4$ **58** is also significantly stronger than HBF$_4$ **33**: the small size of the BF$_4^-$ anion creates high partial charges on the −F substituents so that the very low intrinsic basicity of the −F center increases considerably.

Except for HClO$_4$ **55**, all classical strong mineral acids are in the upper half of the scale. Their relative weakness compared to the acids discussed above is especially noticeable in the case of the hydrogen halides: HCl **2** (p$K_a$ ca. −8 in water[21]) is just slightly stronger than picric acid **1** (p$K_a$ = 0.3 in water[22]), HI **22** (p$K_a$ ca. −10 in water[38]) is more than 5 orders of magnitude weaker than HClO$_4$ (p$K_a$ ca. −10 in water[38]). The reason is obvious: most of the classical mineral acids have small anions and their strength in water comes largely from the efficient solvation of the anions.

An interesting case is HBF$_4$. This acid actually is not supposed to exist. Nevertheless titration of Bu$_4$N$^+$ BF$_4^-$ with acid **64** and afterward with base *t*-BuP$_1$(pyrr) demonstrated the reversibility of the protonation−deprotonation process. The formed complex HF$\cdots$BF$_3$ seems to be stable in solution because of its very low concentration and the extremely low Lewis basicity of DCE. The acid also behaves very consistently: three measurements were carried out with it (see Table 1) and their results are consistent with the measurements not

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[29] Schwesinger, R.; Link, R.; Thiele, G.; Rotter, H.; Honert, D.; Limbach, H.-H.; Männle, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1372–1375.

[30] Kaljurand, I.; Koppel, I. A.; Kütt, A.; Rõõm, E.-I.; Rodima, T.; Koppel, I.; Mishima, M.; Leito, I. *J. Phys. Chem. A* **2007**, *111*, 1245–1250.

[31] Bos, M.; Dahmen, E. A. M. F. *Anal. Chim. Acta* **1973**, *63*, 185–196.

[32] (a) Lipping, L.; Leito, I.; Koppel, I.; Koppel, I. A. *J. Phys. Chem. A* **2009**, *113*, 12972–12978. (b) Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I.; Sonoda, T.; Mishima, M. *J. Am. Chem. Soc.* **2000**, *122*, 5114–5124.

[33] It is expected that the carborane-based superacids are still much stronger.[8,16,32] Our attempts to measure the equilibrium acidity of the unsubstituted HCB$_{11}$H$_{12}$ failed. See the SI and ref 32a.

[34] Vianello, R.; Maksić, Z. B. *New J. Chem.* **2009**, *33*, 739–784. and references cited therein.

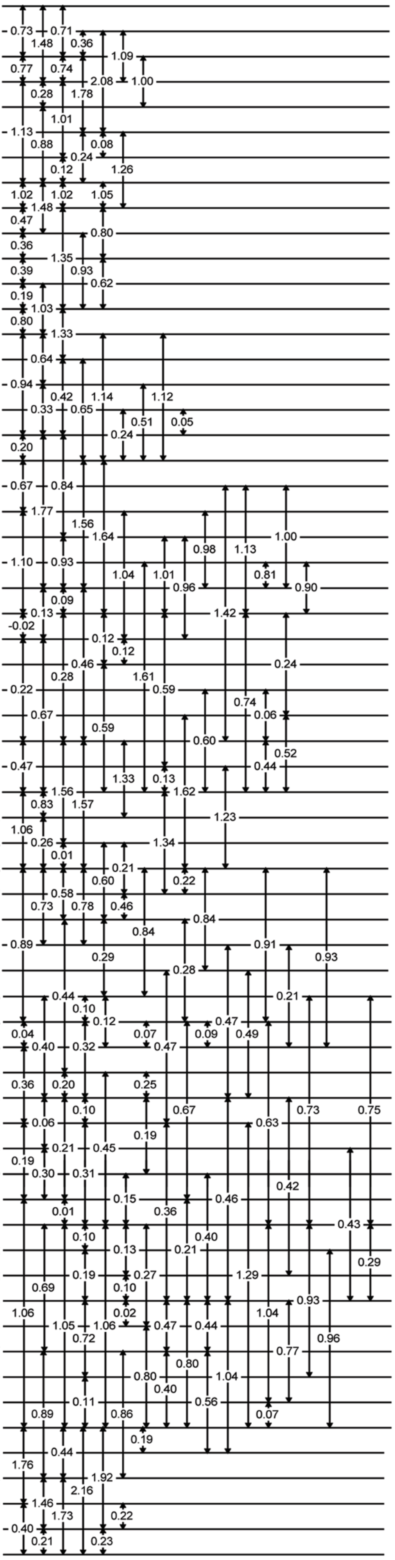
[35] Vianello, R.; Maksić, Z. B. *New J. Chem.* **2008**, *32*, 413–427.

[36] Vianello, R.; Liebman, J. F.; Maksić, Z. B. *Chem.—Eur. J.* **2004**, *10*, 5751–5760.

[37] Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I. *J. Am. Chem. Soc.* **2002**, *124*, 5594–5600.

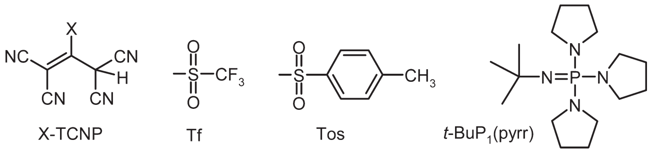
[38] Brownstein, S.; Stillman, A. E. *J. Phys. Chem.* **1959**, *63*, 2061–2062.

**TABLE 1. Equilibrium Acidity Scale Valid in 1,2-Dichloroethane As Solvent (Acidity Increases Downwards)[h]**

| No | Acid | p$K_a$(DCE) | Directly measured $\Delta pK_{ip}$ values in DCE[a] | p$K_a$(MeCN)[b] |
|---|---|---|---|---|
| 1 | Picric acid[c] | 0.0 |  | 11.0 |
| 2 | HCl | -0.4 | | 10.6 |
| 3 | 2,3,4,6-$(CF_3)_5$-$C_6H$-$CH(CN)_2$ | -0.7 | | 10.3 |
| 4 | 4-$NO_2$-$C_6H_4SO_2$NHTos[d] | -1.5 | | 9.6 |
| 5 | $HNO_3$ | -1.7 | | 9.4 |
| 6 | 4-$NO_2$-$C_6H_4SO_2NHSO_2C_6H_4$-4-Cl | -2.4 | | 8.8 |
| 7 | $H_2SO_4$ | -2.5 | | 8.7 |
| 8 | $C_6(CF_3)_5CH(CN)_2$ | -2.6 | | 8.6 |
| 9 | (4-$NO_2$-$C_6H_4$-$SO_2)_2$NH | -3.7 | | 7.7 |
| 10 | 3-$NO_2$-4-Cl-$C_6H_3SO_2NHSO_2C_6H_4$-4-$NO_2$ | -4.1 | | 7.3 |
| 11 | (3-$NO_2$-4-Cl-$C_6H_3SO_2)_2$NH | -4.5 | | 7.0 |
| 12 | HBr | -4.9 | | 6.6 |
| 13 | 4-$NO_2$-$C_6H_4SO_2CH(CN)_2$ | -5.1 | | 6.4 |
| 14 | 2,4,6-$(SO_2F)_3$-Phenol | -5.9 | | 5.7 |
| 15 | 2,4,6-$Tf_3$-Phenol[e] | -6.4 | | 5.2 |
| 16 | $CH(CN)_3$ | -6.5 | | 5.1 |
| 17 | 4-Cl-$C_6H_4$SO(=NTf)NHTos | -6.8 | | 4.9 |
| 18 | $NH_2$-TCNP[f] | -6.8 | | 4.9 |
| 19 | 2,3,5-tricyanocyclopentadiene | -7.0 | | 4.7 |
| 20 | Pentacyanophenol | -7.6 | | 4.2 |
| 21 | 4-Cl-$C_6H_4$SO(=NTf)$NHSO_2C_6H_4$-4-Cl | -7.6 | | 4.1 |
| 22 | HI | -7.7 | | 4.1 |
| 23 | 4-$NO_2$-$C_6H_4SO_2$NHTf | -7.8 | | 4.0 |
| 24 | Me-TCNP | -8.6 | | 3.3 |
| 25 | 3,4-$(MeO)_2$-$C_6H_3$-TCNP | -8.7 | | 3.2 |
| 26 | 4-MeO-$C_6H_4$-TCNP | -8.7 | | 3.2 |
| 27 | $C(CN)_2$=C(CN)OH | -8.8 | | 3.1 |
| 28 | 4-Cl-$C_6H_4$SO(=NTf)$NHSO_2C_6H_4$-4-$NO_2$ | -8.9 | | 3.0 |
| 29 | 2,4-$(NO_2)_2$-$C_6H_3SO_2OH$ | -8.9 | | 3.0 |
| 30 | $C_6F_5CH(Tf)_2$ | -9.0 | | 2.9 |
| 31 | $HB(CN)(CF_3)_3$ | -9.3 | | 2.6 |
| 32 | Ph-TCNP | -9.4 | | 2.5 |
| 33 | $HBF_4$ | -10.3 | | 1.8 |
| 34 | $FSO_2OH$ | -10.5 | | 1.5 |
| 35 | 3-$CF_3$-$C_6H_4$-TCNP | -10.5 | | 1.5 |
| 36 | H-TCNP | -10.7 | | 1.3 |
| 37 | $[C_6H_5SO(=NTf)]_2$NH | -11.1 | | 1.0 |
| 38 | $[(C_2F_5)_2PO]_2$NH | -11.3 | | 0.8 |
| 39 | 2,4,6-$(NO_2)_3$-$C_6H_2SO_2OH$ | -11.3 | | 0.8 |
| 40 | $[C(CN)_2=C(CN)]_2CH_2$ | -11.4 | | 0.8 |
| 41 | TfOH | -11.4 | | 0.7 |
| 42 | $C_6H_5$SO(=NTf)NHTf | -11.5 | | 0.7 |
| 43 | $TfCH(CN)_2$ | -11.6 | | 0.6 |
| 44 | Br-TCNP | -11.8 | | 0.4 |
| 45 | $[C(CN)_2=C(CN)]_2$NH | -11.8 | | 0.3 |
| 46 | 3,5-$(CF_3)_5$-$C_6H_3$-TCNP | -11.8 | | 0.4 |
| 47 | $Tf_2$NH | -11.9 | | 0.3 |
| 48 | 4-Cl-$C_6H_4$SO(=NTf)NHTf | -12.1 | | 0.1 |
| 49 | Cl-TCNP | -12.1 | | 0.1 |
| 50 | $(C_3F_7SO_2)_2$NH | -12.2 | | 0.1 |
| 51 | $(C_4F_9SO_2)_2$NH | -12.2 | | 0.0 |
| 52 | CN-$CH_2$-TCNP | -12.3 | | -0.1 |
| 53 | $(C_2F_5SO_2)_2$NH | -12.3 | | -0.1 |
| 54 | $CF_3$-TCNP | -12.7 | | -0.5 |
| 55 | $HClO_4$ | -13.0 | | -0.7 |
| 56 | $CF_2(CF_2SO_2)_2$NH | -13.1 | | -0.8 |
| 57 | 4-$NO_2$-$C_6H_4$SO(=NTf)NHTf | -13.1 | | -0.8 |
| 58 | $HB(CN)_4$ | -13.3 | | -1.0 |
| 59 | $(FSO_2)_3$CH | -13.6 | | -1.2 |
| 60 | $Tf_2$CH(CN) | -14.9 | | -2.4 |
| 61 | 2,3,4,5-tetracyanocyclopentadiene | -15.1 | | -2.6 |
| 62 | CN-TCNP | -15.3 | | -2.8 |
| 63 | $Tf_3$CH[g] | -16.4 | | -3.7 |
| 64 | $CF_3$SO(=NTf)NHTf[g] | -18 | | -5 |

[a] Directly measured relative acidity values in DCE. [b] Predicted p$K_a$ values of MeCN (see the SI for details). [c] p$K_a$ value of picric acid is arbitrarily set to 0. [d] Tos represents the 4-Me-$C_6H_4SO_2$− group. [e] Tf represents the $CF_3SO_2$− group. [f] X-TCNP represents 2-X-1,1,3,3-tetracyanopropene. [g] Estimated DCE p$K_a$ values, see text. [h] Scheme 1 shows compound and group structures.

**SCHEME 1. Abbreviations for Compounds and Groups Used**



involving $HBF_4$. During this experiment, it is impossible that the acidity of pure HF was measured by mistake (based on the moles of titrants consumed). HF is also such a weak acid (considerably weaker than HCl) that it could not be included into the present scale. We cannot, however, rule out that the acidic species involved was actually a hydrate, such as $H_2O\cdot HBF_4$. The reported p$K_a$ value should therefore be treated with caution.

$CF_3SO(=NTf)NHTf$ **64**—the acidic titrant used in this work to protonate the anions of the strongest acids—is a very strong neutral acid. The Yagupolskii substitution,[37] i.e. replacement of =O by =NTf in aromatic or aliphatic sulfonimides, leads to an acidity increase by 6.4 (**6** and **28**) to 5.3 (**23** and **57**) units. By introducing the Yagupolskii substituent to $Tf_2NH$ **47**, compound **64** is obtained. Taking into account the average acidity increase (5.9 units), the p$K_a$ value of **64** can be estimated as −18 units.

The best-known way to describe acidity of a superacidic medium is the $H_0$ value of Hammett acidity function. The $H_0$ value has been determined for most liquid superacidic media, also for those that have no constant composition, such as mixtures of Brønsted and Lewis acids and mixtures of different Brønsted acids ($HSO_3F$ and $SbF_5$; $CF_3SO_3H$ and $SbF_5$; HF and $HSO_3F$; etc.). The $H_0$ values of the liquid media depend strongly on their actual composition. For example, while HF as a molecule has low acidity, the acidity of liquid HF in terms of $H_0$ is very high: −15.1.[2] This is caused by formation of the highly stable $FHF^-$ ion on dissociation of HF.[2]

Different from the $H_0$ function, the acidity scale of this work characterizes acidity of molecules (similar to the intrinsic GA values in the gas phase) rather than media, and therefore offers information that is complementary to the $H_0$ values. The latter for the different neat superacidic media are determined, in addition to their inherent acidity, also by the variable nonspecific and specific solute−solvent interaction characteristics[23] of the media. Because of this, no good correlation between the p$K_a$ values in DCE and $H_0$ values for individual acids could be expected ($R^2 = 0.37$, $S = 1.30$, with four acids: **7**, **34**, **41**, and **55**).

Correlation of the DCE p$K_a$ values with the gas-phase acidities is also poor (see the SI for details of the correlations). At the same time the comparison of some of the DCE p$K_a$ values measured in this work with the respective MeCN p$K_a$ values shows quite good correlation. The most deviating points in the first case out of 21 points are acids whose anions have rather localized negative charge (HBr **12**, HI **22**) but also some cyanocarbon acids (**19** and **27**) and one sulfonic acid (**29**). In general, it is possible to predict MeCN p$K_a$ values knowing DCE p$K_a$ values at least within ±1.5 p$K_a$ units. This opens the possibility to estimate the MeCN p$K_a$ values of very strong acids that cannot be measured experimentally in MeCN. From the correlation of the gas-phase acidities with DCE p$K_a$ values it seems that acid anions with small size and localized charge (**2**, **5**, **12**, **22**, **41**) behave differently from anions with large size and delocalized charge indicating stabilization of the anion by solvent molecules in the solution phase. The correlations indicate that DCE has ca. 10% better differentiating ability (on a logarithmic scale) than MeCN, but ca. 1.5−2 times lower differentiating ability than the gas phase (see the SI, pages S4 and S5).

## Experimental Section

The UV−vis spectrophotometric titration method used in this work is essentially the same method as described earlier.[22,24] It is based on the UV−vis spectrophotometric titration of a solution of two acids with the solution of a nonabsorbing base *t*-BuP$_1$(pyrr)[39] to obtain the relative acidity of the two compounds. The reversibility of the protonation−deprotonation process was verified with all compounds. Compounds that did not behave reversibly ($HPF_6$, $HAl[OCH(CF_3)_2]_4$) were not included in the scale. For further details see the SI.

**Acknowledgment.** This work was supported by the Grant Nos. 7374 and 8162 from the Estonian Science Foundation and by the target financing projects SF0180061s08 and SF0180089s08 from the Ministry of Education and Science of Estonia. We are indebted to Prof. Takaaki Sonoda and JEMCO Inc. for compounds **47**, **50**, **51**, **53**, and **56**. We are indebted to Prof. O. W. Webster for compounds **19** and **61**.

**Supporting Information Available:** Choosing an anchor compound for the acidity scale, comparison and correlations of DCE p$K_a$ values with IR frequencies ($\nu$NH), MeCN p$K_a$ values, and GA values, homoconjugation, estimate of DCE p$K_a$ values of compounds **63** and **64**, description of failed measurements of some compounds, description of the Δp$K_a$ measurement procedure, MeCN p$K_a$ values of hydrogen halides and a revision of the MeCN p$K_a$ values, description of the origin, purification, and synthesis of used chemicals and solvents, NMR spectra of newly synthesized compounds, and UV−vis spectra of all compounds on the scale that have useful UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(39) Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019–1028.