Excerpt from the Supporting Information to *J. Org. Chem.* **2011**, *76*, 391-395
http://dx.doi.org/10.1021/jo101409p

Revision of pK_a values measured in MeCN

The pK_a measurements in acetonitrile carried out in this work and in ref 5 have considerably increased the reliability of the pK_a values in a continuous self-consistent acidity scale and give considerable support for a revision of the acidic part of the scale. Highly homo- and heteroconjugating sulfonic acids had earlier great influence upon the pK_a values of the stronger acidity area of the scale. By now, many compounds that do not undergo association processes are introduced to this region of the scale and it was discovered that the pK_a values of the problematic compounds introduced a shift into the earlier scale. As a result, we now revise the acetonitrile pK_a values of acids stronger than 4-NO_2-$C_6H_4SO_3$H lowering them by up to 0.32 units. The exact values were found by minimizing the sum of squares of differences between directly measured ΔpK_a values and the assigned pK_a values, as in ref 10. The revised MeCN pK_a values of acids in the stronger acidity area are presented in the following table and should be used instead of those from refs 10 or 15.

Table 3. Acetonitrile pK_a values of acids in the stronger acidity area together with the references to the original sources.

Acid	pK_a	Acid	pK_a	Acid	pK_a
2,4,6-Trinitrophenol (picric acid)	11.00[17]	2,4,6-($SO_2OCH_2CF_3$)$_3$-Phenol	7.97[5]	C_6H_5C(=NTf)NHTf	5.71[15]
4-F-C_6H_4C(=O)NHTf	10.65[10]	1-Naphtalenesulfonic acid (1-$C_{10}H_7SO_3H$)	7.89[15]	$C_6H_5SO_2$NHTf	5.55[15]
2,3,4,5,6-(CF_3)$_5$-Phenol	10.46[11]	4-Cl-3-NO_2-$C_6H_3SO_2$NH- -SO_2-C_6H_4-3-NO_2	7.88[5]	4-F-C_6H_4C(=NTf)NHTf	5.33[15]
2,3,4,6-(CF_3)$_4$-C_6HCH(CN)$_2$	10.45[11]	C_6H_5CH(Tf)$_2$	7.85[15]	4-Cl-C_6H_4-C(=NTf)NHTf	5.24[15]
4-Cl-C6H4C(=O)NHTf	10.36[10]	4-Cl-3-NO_2-$C_6H_3SO_2$NH- -$SO_2C_6H_4$-4-NO_2	7.84[5]	**HBr** (Hydrogen bromide)	5.5
HCl (hydrogen chloride)	10.30	$C_6F_5SO_2NHSO_2C_6H_4$-4-Cl	7.57[5]	2,4,6-(SO_2F)$_3$-Phenol	5.25[15]
(4-Cl-$C_6H_4SO_2$)$_2$NH	10.20[10]	(4-Cl-3-NO_2-$C_6H_3SO_2$)$_2$NH	7.47[5]	($C_6F_5SO_2$)$_2$NH	5.11[5]
4-CF_3-C_6F_4CH(CN)$_2$	10.19[10]	4-chloro-benzenesulfonic acid (4-Cl-C_6H_4-SO_3H)	7.2[15]	4-Cl-$C_6H_4SO_2$NHTf	5.02[15]
2,3,4,5,6-(CF_3)$_5C_6$SH	10.10[5]	$C_6F_5SO_2NHSO_2C_6H_4$-3-NO_2	6.73[5]	4-Cl-C_6H_4SO(=NTf)NHTos	4.81[15]
4-NO_2-$C_6H_4SO_2$NHTos	10.04[10]	3-nitro-benzenesulfonic acid (3-NO_2-$C_6H_4SO_3$H)	6.7[15]	4-NO_2-C_6H_4C(=NTf)NHTf	4.67[15]
4-Cl-3-$NO_2C_6H_3SO_2$NHTos	9.71[10]	$C_6F_5SO_2NHSO_2C_6H_4$-4-NO_2	6.60[5]	2,4,6-Tf_3-Phenol	4.48[15]
4-NO_2-C_6H_4C(=O)NHTf	9.49[10]	4-nitro-benzenesulfonic acid (4-NO_2-$C_6H_4SO_3$H)	6.4[15]	(CN_2)$_2$C=C(CN)OH	4.39
4-NO_2-$C_6H_4SO_2$NH- -$SO_2C_6H_4$-4-Cl	9.17[10]	3-NO_2-$C_6H_4SO_2$CH(CN)$_2$	6.22[5]	4-NO_2-$C_6H_4SO_2$NHTf	4.08[15]
C_6(CF_3)$_5$CH(CN)$_2$	8.86[5]	$C_6F_5SO_2$NH- -$SO_2C_6H_3$-3-NO_2-4-Cl	6.18[5]	4-Cl-C_6H_4SO(=NTf)NHSO$_2$-C_6H_4-4-Cl	4.03[15]
4-Cl-3-NO_2-$C_6H_3SO_2$NH- -$SO_2C_6H_4$-4-Cl	8.80[5]	4-MeO-C_6H_4C(=NTf)NHTf	6.09[15]	2,4-(NO_2)$_2$-$C_6H_3SO_3$H	3.99
p-Toluenesulfonic acid (TosOH, TsOH)	8.5[15]	4-NO_2-$C_6H_4SO_2$CH(CN)$_2$	6.06[5]	2,3,5-tricyano-cyclopentadiene	3.68[15]
(4-NO_2-$C_6H_4SO_2$)$_2$NH	8.19[15]	4-Me-$C_6H_4SO_2$NHTf	5.86[15]	4-Cl-C_6H_4-SO(=NTf)NH- -$SO_2C_6H_4$-4-NO_2	3.33[15]
2,4,6-($SO_2OCH_2CF_2CF_2H$)$_3$-Phenol	8.17[5]	4-Me-C_6H_4C(=NTf)NHTf	5.86[15]	**HI** (Hydrogen iodide)	2.8

Excerpt from the Supporting Information to *J. Org. Chem.* **2011**, *76*, 391-395
http://dx.doi.org/10.1021/jo101409p

References

1. Bos, M.; Dahmen, E. A. M. F. *Anal. Chim. Acta* **1973**, *63*, 185.
2. Davis, M. M. *Acid-Base Behavior in Aprotic Organic Solvents*. National Bureau of Standards, Monograph 105, Washington, D.C., 1968.
3. The term "well-behaving acid" in this work means that the acid and its anion do not form association complexes, do not decompose during the measurements, and at least one of them has an intense UV-Vis spectrum over a wide range of wavelengths.
4. Stoyanov, E.; Kim, K.-C. ; Reed, C. *J. Am. Chem. Soc.* **2006**, *128*, 8500.
5. Leito, I.; Raamat, E.; Kütt, A.; Saame, J.; Kipper, K.; Koppel, I. A.; Koppel, I.; Zhang, M.; Mishima, M.; Yagupolskii, L. M.; Garlyauskayte, R. Yu.; Filatov, A. A. *J. Phys. Chem. A* **2009**, *113*, 8421.
6. Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I. *J. Am. Chem. Soc.* **2002**, *124*, 5594.
7. Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I.; Sonoda, T.; Mishima, M. *J. Am. Chem. Soc.* **2000**, *122*, 5114.
8. Gutowski, K. E.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 12044.
9. 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.; Ignatev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Vlasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047.
10. Kütt, A.; Leito, I.; Kaljurand, I.; Sooväli, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. *J. Org. Chem.* **2006**, *71*, 2829.
11. Kütt, A.; Movchun, V.; Rodima, T.; Dansauer, T.; Rusanov, E. B.; Leito, I.; Kaljurand, I.; Koppel, J.; Pihl, V.; Koppel, I.; Ovsjannikov, G.; Toom, L.; Mishima, M.; Medebielle, M.; Lork, E.; Röschenthaler, G.-V.; Koppel, I. A.; Kolomeitsev, A. A. *J. Org. Chem.* **2008**, *73*, 2607.
12. Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2002**, *67*, 1873.
13. Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 4055.
14. Kütt, A. Ph.D. Thesis, *Studies of acid-base equilibria in non-aqueous media*. Tartu University Press, Tartu. **2008**.
15. Eckert, F.; Leito, I.; Kaljurand, I.; Kütt, A.; Klamt, A.; Diedenhofen, M. *J. Comput. Chem.* **2009**, *30*, 799.
16. Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K. *J. Am. Chem. Soc.* **1961**, *83*, 3927.
17. Kolthoff, I. M.; Chantooni, M. K. *J. Am. Chem. Soc.* **1965**, *87*, 4428.
18. a) Garlyauskayte, R. Yu.; Chernega, A. N.; Michot, C.; Armand, M.; Yagupolskii, Y. L.; Yagupolskii, L. M. *Org. Biomol. Chem.* **2005**, *3*, 2239. (b) Posternak, A. G.; Garlyauskayte, R. Yu.; Polovinko, V. V.; Yagupolskii, L. M.; Yagupolskii, Yu. L. *Org. Biomol. Chem.* **2009**, *7*, 1642. (c) Posternak, A. G.; Garlyauskayte, R. Yu.; Yagupolskii, L. M. *Tetrahedron Lett.* **2009**, *50*, 446.
19. Middleton, W. J.; Little, E. L.; Coffman, D. D.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1958**, *80*, 2795.
20. Middleton, W. J.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1958**, *80*, 2788.
21. Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 558.

Excerpt from the Supporting Information to *J. Org. Chem*. **2011**, *76*, 391-395
http://dx.doi.org/10.1021/jo101409p

22. Kelly, R. B.; Slomp, G.; Caron, E. L. *J. Org. Chem.* **1965**, *30*, 1036.
23. Bernhardt, E.; Finze, M.; Willner, H. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1229.
24. Finze, M.; Bernhardt, E.; Willner, H.; Lehmann, C. V. *J. Am. Chem. Soc.* **2005**, *127*, 10712.
25. Bejan, D.; Willner, H.; Ignatiev, N.; Lehmann, C. W. *Inorg. Chem.* **2008**, *47*, 9085.
26. Yagupolskii, L. M.; Iksanova, S. V.; Kondratenko, N. V. *Zh. Org. Khim.* **1995**, *31*, 747.
27. Piper, J. R.; McCaleb, G. S.; Montgomery, J. A.; Kisliuk, R. L.; Gaumont, Y.; Sirotnak, F. M. *J. Med. Chem.* **1986**, *29*, 1080.
28. Sausen, G. N. US 2847436 19580812, **1958**.
29. Josey, A. D. *J. Org. Chem.* **1964**, *29*, 707.
30. Sun, H.; DiMagno, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 2050.
31. Sausen, G. N.; Engelhardt, V. A.; Middleton, W. J. *J. Am. Chem. Soc.* **1958**, *80*, 2815.
32. Rong, L.; Li, X.; Wang, H.; Shi, D.; Tu, S.; Zhuang, Q. *Synth. Commun.* **2006**, *36*, 2407.
33. Corson, B. B.; Stoughton, R. W. *J. Am. Chem. Soc.* **1928**, *50*, 2825.
34. Troitskaya, V. I.; Trushanina, L. I.; Kopranenkov, V. N.; Lukyanets, E. A.; Yagupolskii, L. M. *Zh. Org. Khim.* **1989**, *25*, 571.
35. Yagupolskii, Y. L.; Pavlenko, N. V.; Lork, E. *Heteroat. Chem.* **1998**, *9*, 565.
36. Yagupolskii, Y. L.; Savina, T. I.; Pavlenko, N. O.; Pankov, A. A.; Pazenok, S. V. *Zh. Obshch. Khim.* **1991**, *61*, 1512.
37. Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 3046.