Supporting information for Koopmans' theorem for acidic protons

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Table S1 Proton orbital energies, all values in eV

name	$\varepsilon^{\mathrm{NEO-HF}}$	$-\varepsilon^{\mathrm{NEO-HF,adj.}}$
water	−25.10	10.99
hydronium ion	−14.11	0.00
formic acid	−23.29	9.18
acetic acid	−23.75	9.64
n-propionic acid	−23.79	9.69
n-butyric acid	−23.82	9.71
isobutyric acid	−23.81	9.70
n-hexanoic acid	−23.83	9.73
n-octanoic acid	−23.84	9.73
n-decanoic acid	−23.84	9.74
phenol	−24.27	10.17
p-toluic acid	−23.79	9.68
glycine	−23.62	9.51
oxalic acid	−22.97	8.86
pyruvic acid	−23.23	9.13

Table S2 Relative (see Eq. 1 in the main article) and absolute energies of the HF calculations without COSMO, all values in eV

name	$\Delta H^{\mathrm{HF}}_{\mathrm{acid}}$	E_{HF}	E_{HF} of anion
water		−2069.69	
hydronium ion		−2077.32	
formic acid	7.75	−5138.68	−5123.31
acetic acid	8.14	−6201.82	−6186.05
n-propionic acid	8.09	−7264.35	−7248.63
n-butyric acid	8.09	−8326.91	−8311.20
isobutyric acid	8.06	−8326.90	−8311.20
n-hexanoic acid	8.11	−10452.05	−10436.32
n-octanoic acid	8.10	−12577.16	−12561.43
n-decanoic acid	8.10	−14702.27	−14686.54
phenol	8.23	−8317.93	−8302.07
p-toluic acid	7.87	−12450.29	−12434.79
glycine	7.96	−7699.71	−7684.13
oxalic acid	7.24	−10246.12	−10231.26
pyruvic acid	7.45	−9270.25	−9255.18

Table S3 Relative (see Eq. 1 in the main article) and absolute energies of the DFT calculations without COSMO, all values in eV

name	$\Delta H^{\mathrm{DFT}}_{\mathrm{acid}}$	E_{DFT}	E_{DFT} of anion
water		−2079.68	
hydronium ion		−2087.13	
formic acid	7.66	−5163.51	−5148.40
acetic acid	8.02	−6233.53	−6218.05
n-propionic acid	7.95	−7303.01	−7287.60
n-butyric acid	7.94	−8372.53	−8357.13
isobutyric acid	7.90	−8372.54	−8357.19
n-hexanoic acid	7.96	−10511.57	−10496.16
n-octanoic acid	7.95	−12650.59	−12635.18
n-decanoic acid	7.95	−14789.61	−14774.20
phenol	8.05	−8365.59	−8350.09
p-toluic acid	7.74	−12519.79	−12504.60
glycine	7.79	−7739.48	−7724.24
oxalic acid	7.15	−10294.84	−10280.24
pyruvic acid	7.32	−9316.89	−9302.12

Table S4 Relative (see Eq. 1 in the main article) and absolute energies of the DFT calculations with COSMO, all values in eV

name	$\Delta H^{\mathrm{DFT-COSMO}}_{\mathrm{acid}}$	E_{DFT}	E_{DFT} of anion
water		−2080.00	
hydronium ion		−2091.15	
formic acid	1.32	−5163.98	−5151.52
acetic acid	1.56	−6233.86	−6221.16
n-propionic acid	1.56	−7303.33	−7290.62
n-butyric acid	1.57	−8372.85	−8360.13
isobutyric acid	1.57	−8372.86	−8360.14
n-hexanoic acid	1.60	−10511.90	−10499.15
n-octanoic acid	1.60	−12650.92	−12638.17
n-decanoic acid	1.60	−14789.95	−14777.19
phenol	1.96	−8365.88	−8352.78
p-toluic acid	1.51	−12520.14	−12507.49
glycine	1.53	−7739.94	−7727.26
oxalic acid	1.08	−10295.42	−10283.20
pyruvic acid	1.17	−9317.34	−9305.01

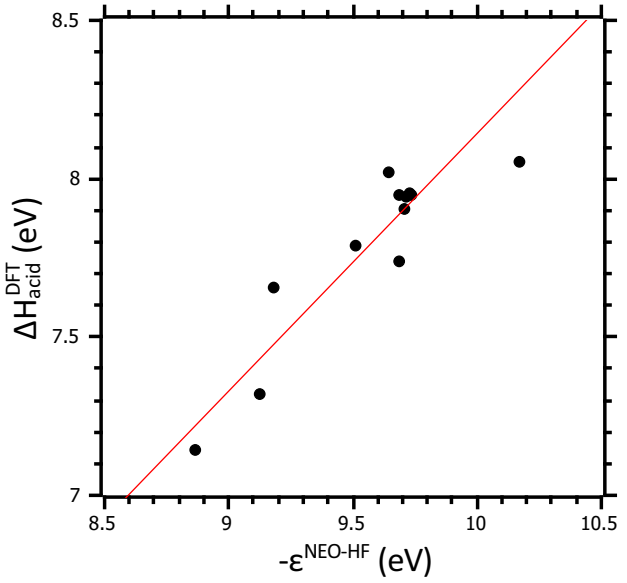

Fig. S1 Adjusted negative NEO-HF proton orbital energies $-\varepsilon^{\mathrm{NEO-HF}}$ correlate with the reaction enthalpy of deprotonation $\Delta H_{\mathrm{acid}}^{\mathrm{DFT}}$ as calculated at the B3-LYP/def2-TZVP level without COSMO. The NEO-Koopmans' correction factor is 0.814 ± 0.003, assuming an intercept of 0 eV.

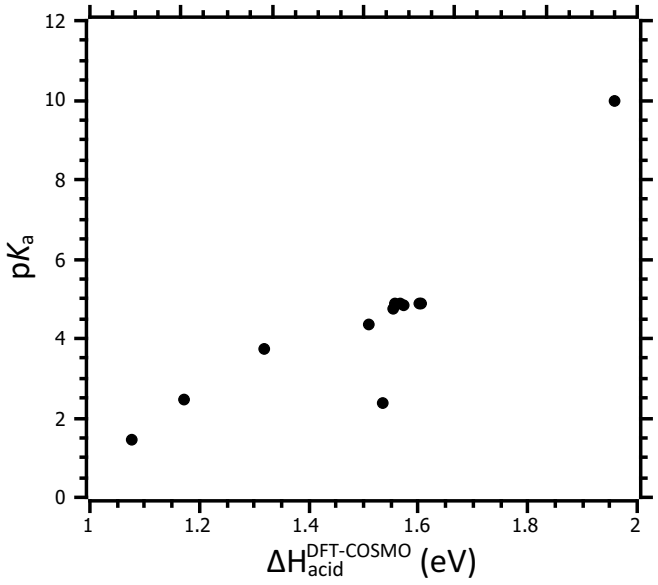

Fig. S2 $\Delta H_{\mathrm{acid}}^{\mathrm{DFT-COSMO}}$ calculated with COSMO correlate well with the negative pK_a

Table S5 Experimantal pK_a values, the proton orbital energies and enthalpy of deprotonation

name	$-\varepsilon^{\mathrm{NEO-HF,adj.}}$ (eV)	ΔH_{acid} with COSMO (eV)	pKa
formic acid	9.18	1.32	3.742 [1]
acetic acid	9.64	1.56	4.756 [2]
n-propionic acid	9.69	1.56	4.88 [3]
n-butyric acid	9.71	1.57	4.82 [4]
isobutyric acid	9.70	1.57	4.86 [5]
n-hexanoic acid	9.73	1.60	4.88 [6]
n-octanoic acid	9.73	1.60	4.895 [7]
n-decanoic acid	9.74	1.60	4.9 [8]
phenol	10.17	1.96	9.99 [5]
p-toluic acid	9.68	1.51	4.34 [9,10]
glycine	9.51	1.53	2.37 [11]
oxalic acid	8.86	1.08	1.46 [12]
pyruvic acid	9.13	1.17	2.45 [11]

References

1 L. Settimo, K. Bellman and R. M. A. Knegtel, *Pharm Res*, 2014, **31**, 1082–1095.
2 W. M. Haynes, *CRC Handbook of Chemistry and Physics, 95th Edition*, CRC Press, 95th edn, 2014.
3 K. G. Latham, A. Ferguson and S. W. Donne, *SN Appl. Sci.*, 2019, **1**, 54.
4 *Physikalische Chemie. Hauptbd.*, ed. P. W. Atkins, Wiley-VCH, 4th edn, 2012.
5 *CRC handbook of tables for organic compound identification*, ed. Z. Rappoport, CRC Press, 3rd edn, 1985.
6 J. A. Riddick, W. B. Bunger and T. K. Sakano, *Organic solvents: physical properties and methods of purification*, J. Wiley & sons, 4th edn, 1986.
7 G. W. Gokel and J. A. Dean, *Dean's handbook of organic chemistry*, McGraw-Hill, 2nd edn, 2004.
8 M. Barratt, *Toxicology in Vitro*, 1996, **10**, 85–94.
9 R. Williams, W. Jencks and F. Westheimer, *Hans Reich's Collection. Bordwell pKa Table. pKa Values in Water Compilation.* (accessed October 2023), `https://organicchemistrydata.org/hansreich/resources/pka/`.
10 F. C. Nachod and J. J. Zuckerman, *Determination of organic structures by physical methods. Vol. 4*, Academic Press, 1971.
11 G. Kortum, W. Vogel, K. Andrussow and International Union of Pure and Applied Chemistry Commission on Electrochemical Data, *Dissociation constants of organic acids in aqueous solution*, Butterworths London, 1961.
12 G. Clayton, *Patty's industrial hygiene and toxicology. 2,A: Toxicology*, Wiley, 3rd edn, 1981.