Supporting Information

Table S1 Calculated energies of substituted ketones CH_3COX, their protonated forms and some reference compounds [a]

	Substituent X	CH_3COX **8a-e** E(DFT) a. u.	CH_3COH^+X E(DFT) a. u.	Rel. basicity kJ mol^{-1}		$\Delta_{10}E$ kJ mol^{-1}	$\Delta_{11}E$ kJ mol^{-1}
				Δ_9E	Δ_9G° [b]		
a	CH_3	−193.2256836	−193.5491603	0	0	0	
b	CH_2F [c]	−292.4883451	−292.7948322	44.6		13.6	58.2
c	CF_3	−491.0415959	−491.3302051 (Z)	91.5	90.1	51.1	142.6
			−491.3257692 (E)				
d	CN	−246.1474231	−246.4312621 (Z)	104.1		45.4	149.5
			−246.4295083 (E)				
e	NO_2	−358.4579626	−358.7329237 (Z)	127.4		34.8	162.2
			−358.7238207 (E)				
	OH	-229.1724354	−229.4837665 (E,Z)	31.9	29.3	−73.4	−41.5

Reference compounds

2-methylpropane	−158.5141761
1-fluoro-2-methylpropane [d]	−257.7820313
1,1,1-trifluoro-2-methylpropane	−456.3495341
2-methylpropanenitrile	−211.4532096
2-nitropropane	−323.7597095
2-propanol	−194.4329568

[a] Calculated at the level B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p). [b] Experimental values obtained from the data of Ref 1. [c] Conformation *sp* on the C–C bond (F near to =O).
[d] Conformation *sc* (F between H and CH_3).

Appendix

Estimation of the resonance contribution to the acidity of acetic acid

This problem was discussed in detail previously and a solution was attempted[9b] using eqn. (12). When the variable groups X in X−OH were not conjugated with the hydroxyl group, the experimental reaction enthalpies $\Delta_{12}H°$ depended empirically on the inductive constants σ_I or better on a linear combination of σ_I and σ_α (the polarizability constant). When the group CH_3CO was introduced as substituent X, deviation from the correlation line is a measure of the resonance effect **R** on the acidity. The resonance effect in the acetate anion was estimated similarly.[9b] The inductive contributions were obtained by subtracting from the total experimental effect. These values were related to methanol. Here they were readjusted to 2-propanol, eqn. (13), and are given in Table 2, first line.

We attempted now to estimate the resonance effect on the acidity from a model close to that used for the basicity. To this purpose, eqn. (14) was advanced with X = CH_3, CN, CF_3 and CH_2F. (With X = NO_2 no stable molecule could be obtained.) The DFT calculated energies of the alcohols $CH_3CHX−OH$ and of their anions $CH_3CHX−O^-$ are given in Table S2, columns 2 and 3, the isodesmic reaction energies $\Delta_{14}E$ of eqn. (14) in column 4.

Table S2 Calculated energies of substituted alcohols $CH_3CHX−OH$ and of their deprotonated forms[a]

Substituent X	$CH_3CHX−OH$ E(DFT) a. u.	$CH_3CHX−O^-$ E(DFT) a. u.	Rel. acidity $\Delta_{14}E$ kJ mol^{-1}	$\Delta_{18}E$ kJ mol^{-1}	$\Delta_{19}E$ kJ mol^{-1}	σ_I
CH_3	−194.4329568	−193.8222911	0	0	0	0
CH_2F [b]	−293.6986081	−293.1028522	−39.2	5.8	−33.4	0.10
CF_3	−492.2636015	−491.6780098	−65.8	12.4	−53.5	0.16
CN	−247.3643777	−246.7870279	−87.5	20.0	−67.5	0.22
acetic acid	−229.1724354	−228.6086418	−123.1	−73.4	−196.5	0.26

[a] Calculated at the level B3LYP/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p). [b] Conformation *ap* on the C−C bond (F opposite to OH).

The plot of $\Delta_{14}E$ vs the inductive constants σ_I is shown in Fig. S1. The values of σ_I for the complex groups $-CH(CH_3)CN$, $-CH(CH_3)CF_3$ and $-CH(CH_3)CH_2F$ were estimated from the standard values[28] for the groups CN, CF_3 and CH_2F, respectively, by multiplying by the fall-off factor of 0.46. They are listed in Table S2, last column.
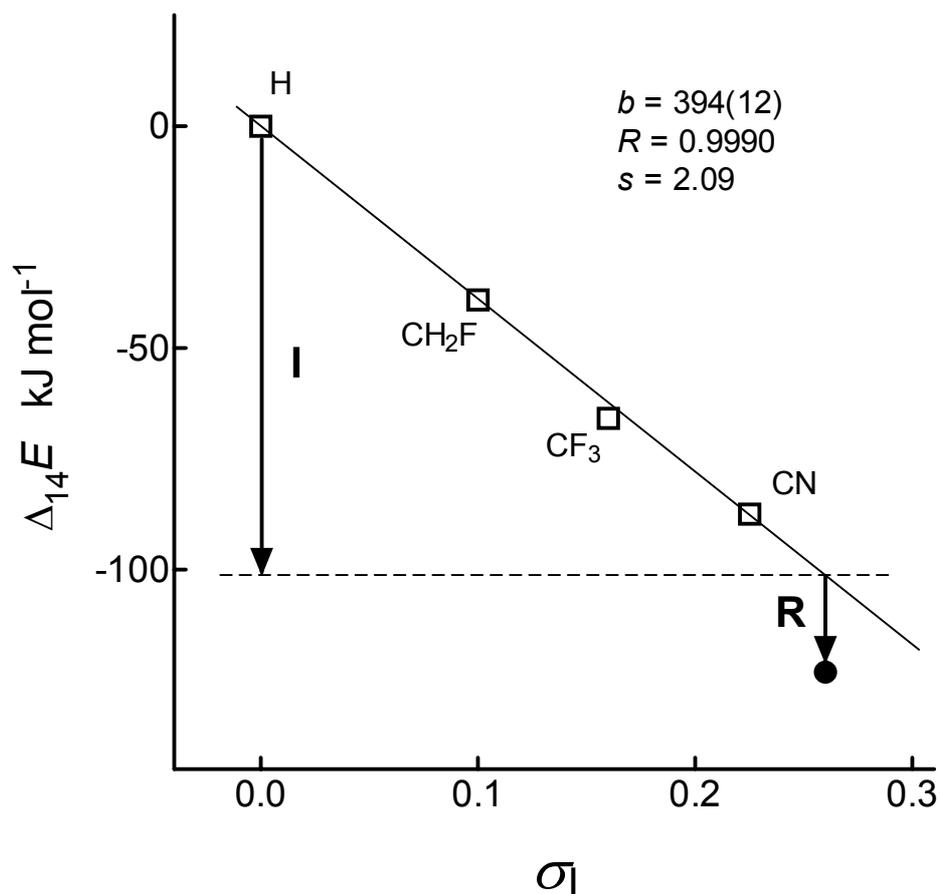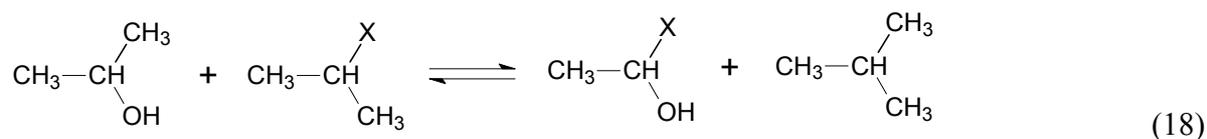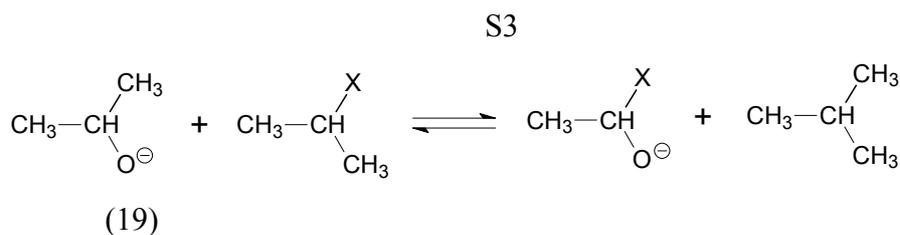

Fig S1 Plot of the calculated relative acidities [eqn. (14)] of substituted alcohols $CH_3CHX-OH$ vs. the inductive constant σ_I, the groups X are given at each point. The point ● belongs to acetic acid, the arrows show the assumed contribution of resonance **R** and of the inductive effect **I**.

Bisection into the effects in the anion and in the neutral acid was attempted by means of the isodesmic reactions of eqns (18) and (19).

$$(18)$$

(19)

The calculated reaction energies $\Delta_{18}E$ and $\Delta_{19}E$ are given in Table S2, columns 5 and 6, respectively. The plot of $\Delta_{19}E$ vs. is shown in Fig. S2.
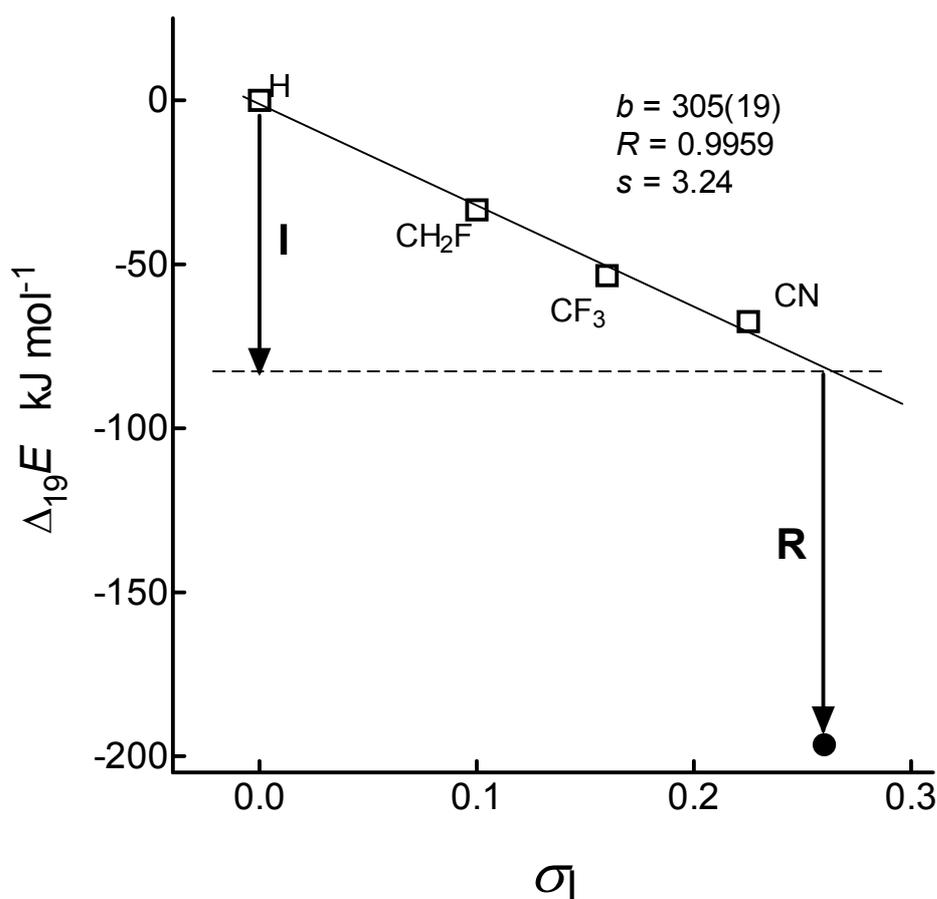

Fig S2 Plot of the calculated stabilization energies of the anions of substituted alcohols CH_3CHX-O^- [isodesmic reaction of eqn. (19)] vs. the inductive constant σ_I, the groups X are denoted at each point. The point ● belongs to acetic acid, the arrows show the assumed contribution of resonance **R** and of the inductive effect **I**.

     The resulting values **R** and **I** for the acidity are given in Table 2, second line. In our opinion they could be somewhat more reliable than the estimates of the line 1, based on a different model [eqn. (13)]. It is true that Figs S1 and S2 are based on a small number of points, on the other hand the correlations are close and the model is homogeneous.