TABLE 8.1 pK_a values for many types of acids *The values in boldface are exact values; the others are approximate, especially above 18 and below −2*[16]

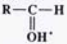
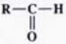
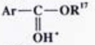
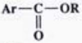
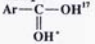
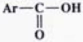
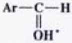
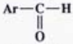
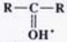
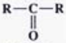
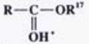
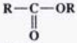
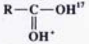
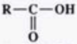
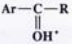
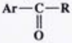
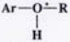
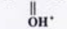
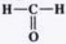
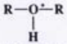
Acid	Base	Approximate pK_a (relative to water)	Ref.
Super acids:			
$HF-SbF_5$	SbF_6^-		19
$FSO_3H-SbF_5-SO_3$			14
FSO_3H-SbF_5			14, 19
FSO_3H	FSO_3^-		14
RNO_2H^+	RNO_2	−12	20
$ArNO_2H^+$	$ArNO_2$	−11	20
$HClO_4$	ClO_4^-	−10	21
HI	I^-	−10	21
$RCNH^+$	RCN	−10	22
 $R-\underset{OH^+}{\underset{\Vert}{C}}-H$	 $R-\underset{O}{\underset{\Vert}{C}}-H$	−10	23
H_2SO_4	HSO_4^-		
HBr	Br^-	−9	21
 $Ar-\underset{OH^+}{\underset{\Vert}{C}}-OR$[17]	 $Ar-\underset{O}{\underset{\Vert}{C}}-OR$	−7.4	20
HCl	Cl^-	−7	21
RSH_2^+	RSH	−7	20
 $Ar-\underset{OH^+}{\underset{\Vert}{C}}-OH$[17]	 $Ar-\underset{O}{\underset{\Vert}{C}}-OH$	−7	24
 $Ar-\underset{OH^+}{\underset{\Vert}{C}}-H$	 $Ar-\underset{O}{\underset{\Vert}{C}}-H$	−7	25
 $R-\underset{OH^+}{\underset{\Vert}{C}}-R$	 $R-\underset{O}{\underset{\Vert}{C}}-R$	−7	9, 22, 26
$ArSO_3H$	$ArSO_3^-$	−6.5	27
 $R-\underset{OH^+}{\underset{\Vert}{C}}-OR$[17]	 $R-\underset{O}{\underset{\Vert}{C}}-OR$	−6.5	20
$ArOH_2^+$	ArOH	−6.4	28
 $R-\underset{OH^+}{\underset{\Vert}{C}}-OH$[17]	 $R-\underset{O}{\underset{\Vert}{C}}-OH$	−6	20
 $Ar-\underset{OH^+}{\underset{\Vert}{C}}-R$	 $Ar-\underset{O}{\underset{\Vert}{C}}-R$	−6	25, 29
 $Ar-\underset{H}{\underset{\vert}{\overset{+}{O}}}-R$	Ar—O—R	−6	28, 30
$CH(CN)_3$	$^-C(CN)_3$	−5	31
Ar_3NH^+	Ar_3N	−5	32
 $H-\underset{OH^+}{\underset{\Vert}{C}}-H$	 $H-\underset{O}{\underset{\Vert}{C}}-H$	−4	33
 $R-\underset{H}{\underset{\vert}{\overset{+}{O}}}-R$	R—O—R	−3.5	22, 30, 34
$R_3COH_2^+$	R_3COH	−2	34
$R_2CHOH_2^+$	R_2CHOH	−2	34, 35
$RCH_2OH_2^+$	RCH_2OH	−2	22, 34, 35
H_3O^+	H_2O	**−1.74**	36

TABLE 8.1 *(Continued)*

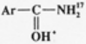
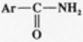
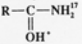
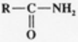
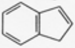
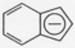
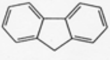
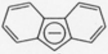
Acid	Base	Approximate pK_a (relative to water)	Ref.
 $\mathrm{Ar{-}\underset{\underset{OH^+}{\Vert}}{C}{-}NH_2^{17}}$	 $\mathrm{Ar{-}\underset{\underset{O}{\Vert}}{C}{-}NH_2}$	−1.5	37
HNO_3	NO_3^-	−1.4	21
 $\mathrm{R{-}\underset{\underset{OH^+}{\Vert}}{C}{-}NH_2^{17}}$	 $\mathrm{R{-}\underset{\underset{O}{\Vert}}{C}{-}NH_2}$	−0.5	37
$Ar_2NH_2^+$	Ar_2NH	1	32
HSO_4^-	SO_4^{2-}	**1.99**	38
HF	F^-	**3.17**	38
HONO	NO_2^-	**3.29**	38
$ArNH_3^+$	$ArNH_2$	3–5	39
$ArNR_2H^+$	$ArNR_2$	3–5	39
RCOOH	$RCOO^-$	4–5	39
$HCOCH_2CHO$	$\mathrm{HCO\overset{\ominus}{\overline{C}}HCHO}$	5	40
$H_2CO_3^{18}$	HCO_3^-	**6.35**	38
H_2S	HS^-	**7.00**	38
ArSH	ArS^-	6–8	41
$CH_3COCH_2COCH_3$	$\mathrm{CH_3CO\overset{\ominus}{\overline{C}}HCOCH_3}$	9	40
HCN	CN^-	9.2	42
NH_4^+	NH_3	**9.24**	38
ArOH	ArO^-	8–11	43
RCH_2NO_2	$\mathrm{R\overset{\ominus}{\overline{C}}HNO_2}$	10	44
R_3NH^+	R_3N	10–11	39
RNH_3^+	RNH_2	10–11	39
HCO_3^-	CO_3^{2-}	**10.33**	38
RSH	RS^-	10–11	41
$R_2NH_2^+$	R_2NH	11	39
$NCCH_2CN$	$\mathrm{NC\overset{\ominus}{\overline{C}}HCN}$	11	40, 45
CH_3COCH_2COOR	$\mathrm{CH_3CO\overset{\ominus}{\overline{C}}HCOOR}$	11	40
$CH_3SO_2CH_2SO_2CH_3$	$\mathrm{CH_3SO_2\overset{\ominus}{\overline{C}}HSO_2CH_3}$	12.5	46
$EtOOCCH_2COOEt$	$\mathrm{EtOOC\overset{\ominus}{\overline{C}}HCOOEt}$	13	40
CH_3OH	CH_3O^-	15.2	47, 48
H_2O	OH^-	**15.74**	49
		16	50
RCH_2OH	RCH_2O^-	16	47
RCH_2CHO	$\mathrm{R\overset{\ominus}{\overline{C}}HCHO}$	16	51
R_2CHOH	R_2CHO^-	16.5	47
R_3COH	R_3CO^-	17	47
$RCONH_2$	$RCONH^-$	17	52
$RCOCH_2R$	$\mathrm{RCO\overset{\ominus}{\overline{C}}HR}$	19–20	53
		20	54, 55
		23	54, 55
$ROOCCH_2R$	$\mathrm{ROOC\overset{\ominus}{\overline{C}}HR}$	24.5	40

TABLE 8.1 *(Continued)*

Acid	Base	Approximate pK_a (relative to water)	Ref.
RCH_2CN	$R\overset{\ominus}{\bar{C}}HCN$	25	40, 56
$HC\equiv CH$	$HC\equiv C^-$	25	57
Ar_3CH	Ar_3C^-	31.5	54, 58
Ar_2CH_2	Ar_2CH^-	33.5	54, 58
H_2	H^-	35	59
NH_3	NH_2^-	38	60
$PhCH_3$	$PhCH_2^-$	40	61
$CH_2{=}CHCH_3$	$[CH_2 \mathrel{\overset{\cdots}{-}} CH \mathrel{\overset{\cdots}{-}} CH_2]^-$	43	62
PhH	Ph^-	43	63
$CH_2{=}CH_2$	$CH_2{=}CH^-$	44	64
cyclo-C_3H_6	cyclo-$C_3H_5^-$	46	65
CH_4	CH_3^-	48	66
C_2H_6	$C_2H_5^-$	50	67
$(CH_3)_2CH_2$	$(CH_3)_2CH^-$	51	67
$(CH_3)_3CH$	$(CH_3)_3C^-$	—	68

[16] In this table we do not give pK_a values for individual compounds (with a few exceptions), only average values for functional groups. Extensive tables of pK values for many carboxylic and other acids and amines are given in Ref. 39. Values for more than 5500 organic acids are given in Serjeant; Dempsey *Ionisation Constants of Organic Acids in Aqueous Solution*; Pergamon: Elmsford, NY, 1979; Kortüm; Vogel; Andrussow *Dissociation Constants of Organic Acids in Aqueous Solution*; Butterworth: London, 1961. The index in the 1979 volume covers both volumes. Kortüm; Vogel; Andrussow *Pure Appl. Chem.* **1960,** *1*, 190-536 give values for 631 carboxylic acids and 110 phenols. Ref. 20 gives hundreds of values for very strong acids (very weak bases). Perrin *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworth: London, 1965, and Supplement, 1972 list pK values for more than 7000 amines and other bases. Collumeau *Bull. Soc. Chim. Fr.* **1968,** 5087-5112 gives pK values for about 800 acids and bases. Bordwell *Acc. Chem. Res.* **1988,** *21*, 456-463 gives values for more than 300 acids in dimethyl sulfoxide. For inorganic acids and bases, see Perrin, Ref. 42, *Pure Appl. Chem.* **1969,** *20*, 133-236.

[17] Carboxylic acids, esters, and amides are shown in this table to be protonated on the carbonyl oxygen. There has been some controversy on this point, but the weight of evidence is in that direction. See, for example, Katritzky; Jones *Chem. Ind. (London)* **1961,** 722; Ottenheym; van Raayen; Smidt; Groenewege; Veerkamp *Recl. Trav. Chim. Pays-Bas* **1961,** *80*, 1211; Stewart; Muenster *Can. J. Chem.* **1961,** *39*, 401; Smith; Yates *Can. J. Chem.* **1972,** *50*, 771; Benedetti; Di Blasio; Baine *J. Chem. Soc. Perkin Trans. 2* **1980,** 500; Ref. 8; Homer; Johnson, in Zabicky *The Chemistry of Amides*; Wiley: New York, 1970, pp. 188-197. It has been shown that some amides protonate at nitrogen: see Perrin *Acc. Chem. Res.* **1989,** *22*, 268-275. For a review of alternative proton sites, see Liler *Adv. Phys. Org. Chem.* **1975,** *11*, 267-392.

[18] This value includes the CO_2 usually present. The value for H_2CO_3 alone is 3.9 (Ref. 21).

[19] Brouwer; van Doorn *Recl. Trav. Chim. Pays-Bas* **1972,** *91*, 895; Gold; Laali; Morris; Zdunek *J. Chem. Soc., Chem. Commun.* **1981,** 769; Sommer; Canivet; Schwartz; Rimmelin *Nouv. J. Chim.* **1981,** *5*, 45.

[20] Arnett *Prog. Phys. Org. Chem.* **1963,** *1*, 223-403, pp. 324-325.

[21] Bell, Ref. 1.

[22] Deno; Wisotsky *J. Am. Chem. Soc.* **1963,** *85*, 1735; Deno; Gaugler; Wisotsky *J. Org. Chem.* **1966,** *31*, 1967.

[23] Levy; Cargioli; Racela *J. Am. Chem. Soc.* **1970,** *92*, 6238. See, however, Brouwer; van Doorn *Recl. Trav. Chim. Pays-Bas* **1971,** *90*, 1010.

[24] Stewart; Granger *Can. J. Chem.* **1961,** *39*, 2508.

[25] Yates; Stewart *Can. J. Chem.* **1959,** *37*, 664; Stewart; Yates *J. Am. Chem. Soc.* **1958,** *80*, 6355.

[26] Lee *Can. J. Chem.* **1970,** *48*, 1919.

[27] Cerfontain; Koeberg-Telder; Kruk *Tetrahedron Lett.* **1975,** 3639.

[28] Arnett; Wu *J. Am. Chem. Soc.* **1960,** *82*, 5660; Koeberg-Telder; Lambrechts; Cerfontain *Recl. Trav. Chim. Pays-Bas* **1983,** *102*, 293.

[29] Fischer; Grigor; Packer; Vaughan *J. Am. Chem. Soc.* **1961,** *83*, 4208.

[30] Arnett; Wu *J. Am. Chem. Soc.* **1960,** *82*, 4999.

[31] Boyd *J. Phys. Chem.* **1963,** *67*, 737.

[32] Arnett; Quirk; Burke *J. Am. Chem. Soc.* **1970,** *92*, 1260.

[33] McTigue; Sime *Aust. J. Chem.* **1963,** *16*, 592.

[34] Deno; Turner *J. Org. Chem.* **1966,** *31*, 1969.

[35] Lee; Demchuk *Can. J. Chem.* **1987,** *65*, 1769; Chandler; Lee *Can. J. Chem.* **1990,** *68*, 1757.

[36] For a discussion, see Campbell; Waite *J. Chem. Educ.* **1990,** *67*, 386.

[37] Cox; Druet; Klausner; Modro; Wan; Yates *Can. J. Chem.* **1981,** *59*, 1568; Grant; McTigue; Ward *Aust. J. Chem.* **1983,** *36*, 2211.