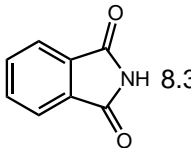
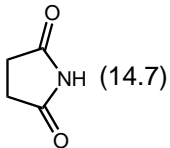
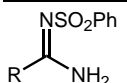
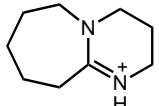
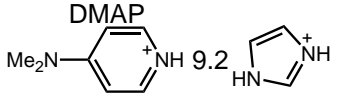
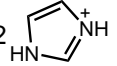

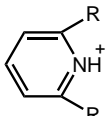
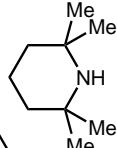
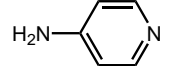
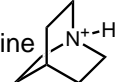
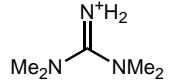
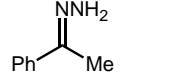
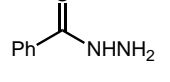
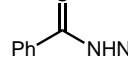
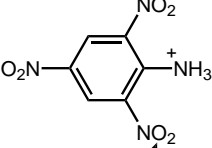
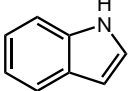
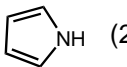
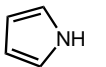
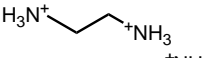
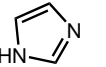
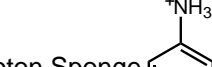
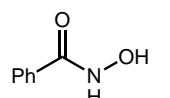
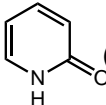
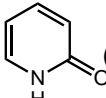
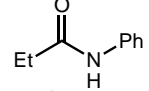
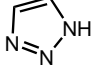
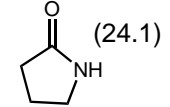
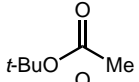
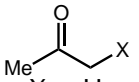
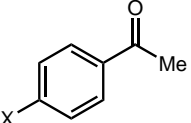
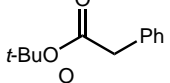
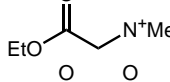
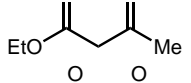

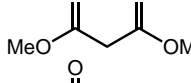
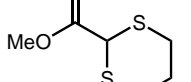
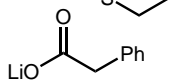
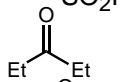

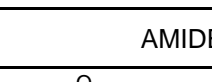
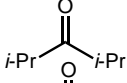
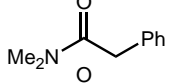
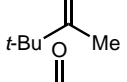
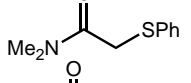
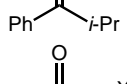
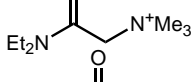
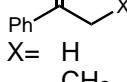
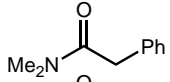
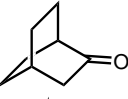
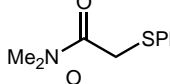
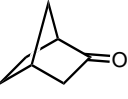
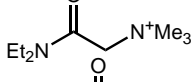
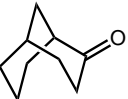
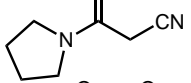
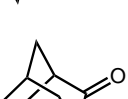
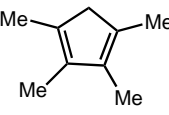
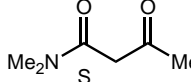
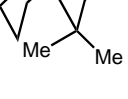
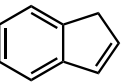





Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	
<b>PROTONATED NITROGEN</b>			<b>AMINES</b>			<b>IMIDES</b>			<b>AMIDINES</b>			
N <sup>+</sup> H <sub>4</sub>	9.2	(10.5)	HN <sub>3</sub>	4.7	(7.9)		8.30					
EtN <sup>+</sup> H <sub>3</sub>	10.6		NH <sub>3</sub>	38	(41)				R= Me	(17.3)		
<i>i</i> -Pr <sub>2</sub> N <sup>+</sup> H <sub>2</sub>	11.05		<i>i</i> -Pr <sub>2</sub> NH	(36 THF))					R= Ph	(15.0)		
Et <sub>3</sub> N <sup>+</sup> H	10.75	(9.00)	TMS <sub>2</sub> NH	26(THF)	(30)	Ac <sub>2</sub> NH		(17.9)	<b>PROTONATED HETEROCYCLES</b>			
PhN <sup>+</sup> H <sub>3</sub>	4.6	(3.6)	PhNH <sub>2</sub>		(30.6)	<b>SULFONAMIDE</b>			DBU		(12) (estimate)	
PhN <sup>+</sup> (Me) <sub>2</sub> H	5.20	(2.50)	Ph <sub>2</sub> NH		(25.0)	MeSO <sub>2</sub> NH <sub>2</sub>		(17.5)	DMAP		9.2	
Ph <sub>2</sub> N <sup>+</sup> H <sub>2</sub>	0.78		NCNH <sub>2</sub>		(16.9)	PhSO <sub>2</sub> NH <sub>2</sub>		(16.1)	Me <sub>2</sub> N-		6.95	
2-naphthal-N <sup>+</sup> H <sub>3</sub>	4.16				(44)	CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub>	6.3	(9.7)				
H <sub>2</sub> NN <sup>+</sup> H <sub>3</sub>	8.12		TMP		(37)	MeSO <sub>2</sub> NHPh		(12.9)	R= H (PPTS)	5.21	(3.4)	
HON <sup>+</sup> H <sub>3</sub>	5.96				(26.5)	<b>GUANIDINIUM, HYDRAZONES, -IDES, &amp; -INES</b>			<i>t</i> -Bu	4.95	(0.90)	
Quinuclidine	11.0	(9.80)	<b>AMIDES &amp; CARBAMATES</b>					(13.6)	Me	6.75	(4.46)	
Morpholine		N <sup>+</sup> H <sub>2</sub>	R-C(=O)-NH <sub>2</sub>					(21.6)	Cl, H	0.72		
N-Me morpholine	7.38		R= H		(23.5)			(18.9)	<b>HETEROCYCLES</b>			
	-9.3		CH <sub>3</sub>	15.1	(25.5)	PhSO <sub>2</sub> NHNH <sub>2</sub>		(17.2)		(20.95)		
DABCO		N <sup>+</sup> H	Ph		(23.3)	PhNHNHPh		(26.1)		(23.0)		(18.6)
	2.97, 8.82 (2.97, 8.93)		CF <sub>3</sub>		(17.2)	<b>HYDROXAMIC ACID</b>				(17.0)	1,2,3 triazole	
	6.90, 9.95		NH <sub>2</sub> (urea)		(26.9)		8.88	(13.7) (NH)		(13.9)		
Proton Sponge		N <sup>+</sup> H <sub>3</sub> , N <sup>+</sup> H <sub>3</sub>	OEt		(24.8)							
PhCN <sup>+</sup> H	-10				(21.6)							
				(24.1)								
				12	(20.5)							

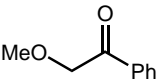
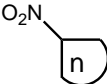
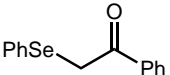
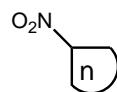
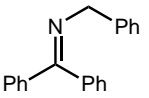
\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)
<b>HYDROCARBONS</b>			<b>ESTERS</b>			<b>KETONES</b>					
(Me) <sub>3</sub> CH	53			24.5	(30.3)						
(Me) <sub>2</sub> CH <sub>2</sub>	51				(23.6)	X= H		(26.5)	X= H		(24.7)
CH <sub>2</sub> =CH <sub>2</sub>	50					Ph		(19.8)	OMe		(25.7)
CH <sub>4</sub>	48	(56)			(20.0)	SPh		(18.7)	NMe <sub>2</sub>		(27.5)
	46				(20.0)	COCH <sub>3</sub>	9	(13.3)	Br		(23.8)
CH <sub>2</sub> =CHCH <sub>3</sub>	43	(44)		11	(14.2)	SO <sub>2</sub> Ph		(15.1)	CN		(22.0)
PhH	43						19-20	(27.1)			
PhCH <sub>3</sub>	41	(43)		13	(15.7)			(28.3)	n= 4		(25.1)
Ph <sub>2</sub> CH <sub>2</sub>	33.5	(32.2)			(20.9)			(27.7)	5		(25.8)
Ph <sub>3</sub> CH	31.5	(30.6)				Ph		(26.3)	6		(26.4)
HCCH	24				[30.2 (THF)]				7		(27.7)
PhCCH	23	(28.8)	<b>AMIDES</b>			X= H		(24.7)	8		(27.4)
XC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>					(26.6)	CH <sub>3</sub>		(24.4)			(28.1)
X= p-CN		(30.8)			(25.9)	Ph		(17.7)			(29.0)
p-NO <sub>2</sub>		(20.4)			(24.9)	COCH <sub>3</sub>		(12.7)			(25.5)
p-COPh		(26.9)			(17.2)	COPh		(13.3)			(25.5)
		(26.1)			(18.2)	CO <sub>2</sub> Et		(22.7)			(32.4)
	20	(20.1)			(25.7)	CN		(10.2)			
	15	(18.0)				F		(21.6)			
H <sub>2</sub>	~36					OMe		(22.85)			
						OPh		(21.1)			
						SPh		(16.9)			
						SePh		(18.6)			
						NPh <sub>2</sub>		(20.3)			
						N <sup>+</sup> Me <sub>3</sub>		(14.6)			
						NO <sub>2</sub>		(7.7)			
						SO <sub>2</sub> Ph		(11.4)			

\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)
<b>NITRILES</b>			<b>SULFIDES</b>			<b>SULFOXIDES</b>			<b>SULFONES</b>		
NC-CH <sub>2</sub> -X			PhSCH <sub>2</sub> X								
X= H		(31.3)	X= Ph		(30.8)	X= H		(35.1)	X= H		(29.0)
CH <sub>3</sub>		(32.5)	CN		(20.8)			(29.0)	CH <sub>3</sub>		(31.0)
Ph		(21.9)	COCH <sub>3</sub>		(18.7)	X= Ph		(27.2)	<i>t</i> -Bu		(31.2)
COPh		(10.2)	COPh		(16.9)			(18.2)	Ph		(23.4)
CONR <sub>2</sub>		(17.1)	NO <sub>2</sub>		(11.8)	X= H		(33)	CH=CH <sub>2</sub>		(22.5)
CO <sub>2</sub> Et		(13.1)	SPh		(30.8)	Ph		(27.2)	CH=CHPh		(20.2)
CN	11	(11.1)	SO <sub>2</sub> Ph		(20.3)			(24.5)	CCH		(22.1)
OPh		(28.1)	SO <sub>2</sub> CF <sub>3</sub>		(11.0)	<b>SULFONIUM</b>			CCPh		(17.8)
N <sup>+</sup> Me <sub>3</sub>		(20.6)	POPh <sub>2</sub>		(24.9)	Me <sub>3</sub> S <sup>+</sup> =O		(18.2)	COPh		(11.4)
SPh		(20.8)	MeSCH <sub>2</sub> SO <sub>2</sub> Ph		(23.4)			(16.3)	COMe		(12.5)
SO <sub>2</sub> Ph		(12.0)	PhSCHPh <sub>2</sub>		(26.7)	<b>SULFIMIDES &amp; SULFOXIMINES</b>			OPh		(27.9)
<b>HETERO-AROMATICS</b>			(PhS) <sub>3</sub> CH		(22.8)			(27.6)	N <sup>+</sup> Me <sub>3</sub>		(19.4)
		(28.2)	(PrS) <sub>3</sub> CH		(31.3)			(30.7)	CN		(12.0)
		(30.1)			(23.0)	R= Me		(24.3)	NO <sub>2</sub>		(7.1)
		(26.7)			(23.0)	Et		(24.0)	SMe		(23.5)
		(25.2)	X= Ph		(30.7)	<i>i</i> -Pr		(23.6)	SPh		(20.5)
		(30.2)	CO <sub>2</sub> Me		(20.8)	Me		(22.9)	SO <sub>2</sub> Ph		(12.2)
		(30.0)	CN		(19.1)	Ph		(20.7)	PPh <sub>2</sub>		(20.2)
			RSCH <sub>2</sub> CN					(33)			(22.3)
			R= Me		(24.3)			(33)			(31.1)
			Et		(24.0)			(14.4)			(18.8)
			<i>i</i> -Pr		(23.6)			(14.4)			(21.8)
			<i>t</i> -Bu		(22.9)			(20.7)			(21.8)
			PhSCH=CHCH <sub>2</sub> SPh		(26.3)			(20.7)			(26.6)
			BuSH	10-11	(17.0)			(20.7)			(26.6)
			PhSH	≈7	(10.3)			(20.7)			(32.8)
								(20.7)	(PhSO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> Me		(14.3)

\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	Substrate	pKa	H <sub>2</sub> O (DMSO)	REFERENCES
<b>ETHERS</b>			<b>PHOSPHONIUM</b>			<b>NITRO</b>			DMSO: JACS <u>97</u> , 7007 (1975) JACS <u>97</u> , 7160 (1975) JACS <u>97</u> , 442 (1975) JACS <u>105</u> , 6188 (1983) JOC <u>41</u> , 1883 (1976) JOC <u>41</u> , 1885 (1976) JOC <u>41</u> , 2786 (1976) JOC <u>41</u> , 2508 (1976) JOC <u>42</u> , 1817 (1977) JOC <u>42</u> , 321 (1977) JOC <u>42</u> , 326 (1977) JOC <u>43</u> , 3113 (1978) JOC <u>43</u> , 3095 (1978) JOC <u>43</u> , 1764 (1978) JOC <u>45</u> , 3325 (1980) JOC <u>45</u> , 3305 (1980) JOC <u>45</u> , 3884 (1980) JOC <u>46</u> , 4327 (1981) JOC <u>46</u> , 632 (1981) JOC <u>47</u> , 3224 (1982) JOC <u>47</u> , 2504 (1982) Acc. Chem. Res. <u>21</u> , 456 (1988) Unpublished results of F. Bordwell
CH <sub>3</sub> OPh	(49)		P <sup>+</sup> H <sub>4</sub>	-14		RNO <sub>2</sub>			
MeOCH <sub>2</sub> SO <sub>2</sub> Ph	(30.7)		MeP <sup>+</sup> H <sub>3</sub>	2.7		R = CH <sub>3</sub>	≈10 (17.2)		
PhOCH <sub>2</sub> SO <sub>2</sub> Ph	(27.9)		Et <sub>3</sub> P <sup>+</sup> H	9.1		CH <sub>2</sub> Me	(16.7)		
PhOCH <sub>2</sub> CN	(28.1)		Ph <sub>3</sub> P <sup>+</sup> CH <sub>3</sub>	(22.4)		CHMe <sub>2</sub>	(16.9)		
	(21.1)		Ph <sub>3</sub> P <sup>+</sup> <i>i</i> -Pr	(21.2)		CH <sub>2</sub> Ph	(12.2)		
<b>SELENIDES</b>			<b>PHOSPONATES &amp; PHOSPHINE OXIDES</b>						
	(18.6)		(EtO) <sub>2</sub> P(=O)CH <sub>2</sub> X			n = 3	(26.9)		
PhSeCHPh <sub>2</sub>	(27.5)		X = Ph	(27.6)		4	(17.8)		
(PhSe) <sub>2</sub> CH <sub>2</sub>	(31.3)		CN	(16.4)		5	(16.0)		
PhSeCH <sub>2</sub> Ph	(31.0)		CO <sub>2</sub> Et	(18.6)		6	(17.9)		
PhSeCH=CHCH <sub>2</sub> SePh	(27.2)		Cl	(26.2)		7	(15.8)		
<b>AMMONIUM</b>				SiMe <sub>3</sub>	(28.8)	<b>IMINES</b>			
Me <sub>3</sub> N <sup>+</sup> CH <sub>2</sub> X			X = SPh	(24.9)			(24.3)		
X = CN	(20.6)		CN	(16.9)		Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts Streitwieser, JOC 1991, 56, 1989			
SO <sub>2</sub> Ph	(19.4)		<b>PHOSPHINES</b>			Water: Advanced Org. Chem., 3rd Ed. J. March (1985) Unpublished results of W. P. Jencks			
COPh	(14.6)		Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub>	(29.9)		THF: JACS <u>110</u> , 5705 (1988)			
CO <sub>2</sub> Et	(20.6)		Ph <sub>2</sub> PCH <sub>2</sub> SO <sub>2</sub> Ph	(20.3)					
CONEt <sub>2</sub>	(24.9)								

\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.