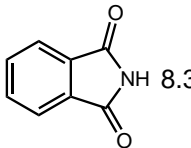
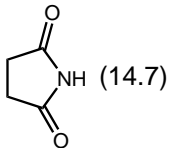
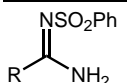
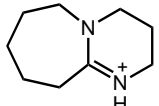
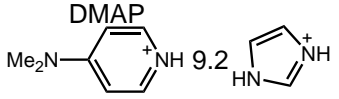
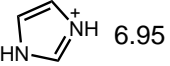
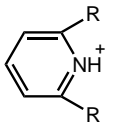
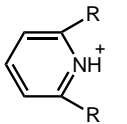
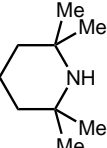
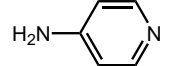
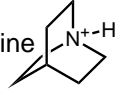
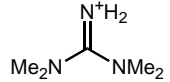
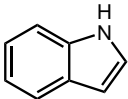
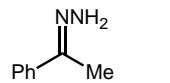
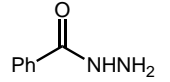
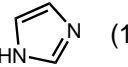
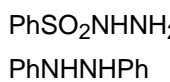
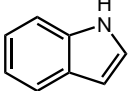
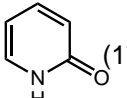
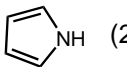
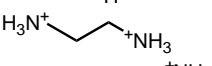
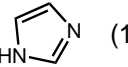
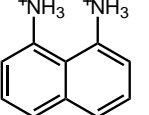
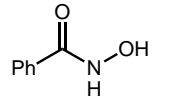
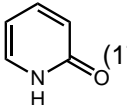
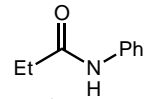
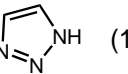
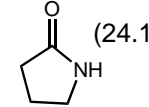
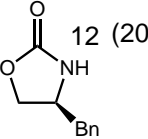
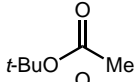
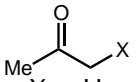
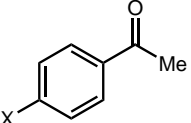
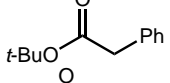
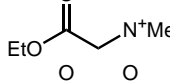
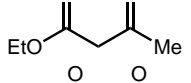

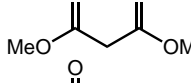
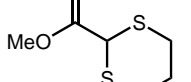
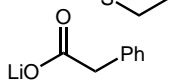
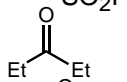

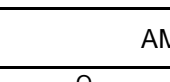
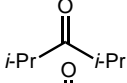

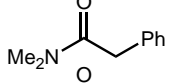
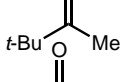
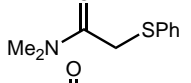
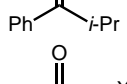
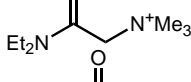
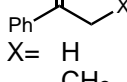
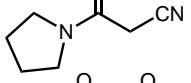
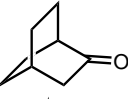
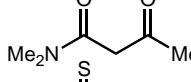
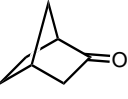
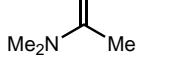
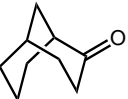
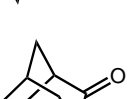
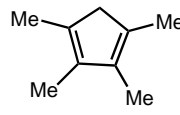
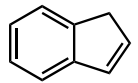



Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O(DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
INORGANIC ACIDS			CARBOXYLIC ACIDS			ALCOHOLS			PROTONATED SPECIES		
H ₂ O	15.7	(32)				HOH	15.7	(31.2)			-12.4
H ₃ O ⁺	-1.7		X= CH ₃	4.76	(12.3)	MeOH	15.54	(27.9)			-7.8
H ₂ S	7.00		CH ₂ NO ₂	1.68		<i>i</i> -PrOH	16.5	(29.3)			-6.2
HBr	-9.00	(0.9)	CH ₂ F	2.66		<i>t</i> -BuOH	17	(29.4)			-6.5
HCl	-8.0	(1.8)	CH ₂ Cl	2.86		<i>c</i> -hex ₃ COH	24				-3.8
HF	3.17	(15)	CH ₂ Br	2.86		CF ₃ CH ₂ OH	12.5	(23.5)			-2.05
HOCl	7.5		CH ₂ I	3.12		(CF ₃) ₂ CHOH		(17.9)			-2.2
HClO ₄	-10		CHCl ₂	1.29		C ₆ H ₅ OH	9.95	(18.0)			-1.8
HCN	9.4	(12.9)	CCl ₃	0.65		<i>m</i> -O ₂ NC ₆ H ₄ OH	8.35				0.79
HN ₃	4.72	(7.9)	CF ₃	-0.25		<i>p</i> -O ₂ NC ₆ H ₄ OH	7.14	(10.8)			
HSCN	4.00		H	3.77		<i>p</i> -OMeC ₆ H ₄ OH	10.20	(19.1)			
H ₂ SO ₃	1.9, 7.21		HO	3.6, 10.3		2-naphthol		(17.1)			
H ₂ SO ₄	-3.0, 1.99		C ₆ H ₅	4.2	(11.1)	OXIMES & HYDROXAMIC ACIDS					
H ₃ PO ₄	2.12, 7.21, 12.32		<i>o</i> -O ₂ NC ₆ H ₄	2.17			11.3	(20.1)			
HNO ₃	-1.3		<i>m</i> -O ₂ NC ₆ H ₄	2.45			8.88	(13.7)			
HNO ₂	3.29		<i>p</i> -O ₂ NC ₆ H ₄	3.44				(18.5)			
H ₂ CrO ₄	-0.98, 6.50		<i>o</i> -ClC ₆ H ₄	2.94		PEROXIDES					
CH ₃ SO ₃ H	-2.6	(1.6)	<i>m</i> -ClC ₆ H ₄	3.83		MeOOH	11.5				
CF ₃ SO ₃ H	-14	(0.3)	<i>p</i> -ClC ₆ H ₄	3.99		CH ₃ CO ₃ H	8.2				
NH ₄ Cl	9.24		<i>p</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄	1.37							
B(OH) ₃	9.23		<i>p</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄	3.43							
HOOH	11.6		<i>p</i> -OMeC ₆ H ₄	4.47							
			R= H	4.25							
			<i>trans</i> -CO ₂ H	3.02, 4.38							
			<i>cis</i> -CO ₂ H	1.92, 6.23							

*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
PROTONATED NITROGEN			AMINES			IMIDES			AMIDINES		
N ⁺ H ₄	9.2	(10.5)	HN ₃	4.7	(7.9)		8.30				
EtN ⁺ H ₃	10.6		NH ₃	38	(41)				R= Me	(17.3)	
<i>i</i> -Pr ₂ N ⁺ H ₂	11.05		<i>i</i> -Pr ₂ NH	(36 THF))					R= Ph	(15.0)	
Et ₃ N ⁺ H	10.75	(9.00)	TMS ₂ NH	26(THF)	(30)	Ac ₂ NH		(17.9)	PROTONATED HETEROCYCLES		
PhN ⁺ H ₃	4.6	(3.6)	PhNH ₂		(30.6)	SULFONAMIDE			DBU		(12) (estimate)
PhN ⁺ (Me) ₂ H	5.20	(2.50)	Ph ₂ NH		(25.0)	MeSO ₂ NH ₂		(17.5)	DMAP		9.2
Ph ₂ N ⁺ H ₂	0.78		NCNH ₂		(16.9)	PhSO ₂ NH ₂		(16.1)	Me ₂ N		6.95
2-naphthal-N ⁺ H ₃	4.16				(44)	CF ₃ SO ₂ NH ₂	6.3	(9.7)			
H ₂ NN ⁺ H ₃	8.12		TMP		(37)	MeSO ₂ NHPh		(12.9)	R= H (PPTS)	5.21	(3.4)
HON ⁺ H ₃	5.96				(26.5)	GUANIDINIUM, HYDRAZONES, -IDES, & -INES			<i>t</i> -Bu	4.95	(0.90)
Quinuclidine		11.0	AMIDES & CARBAMATES					(13.6)	Me	6.75	(4.46)
Morpholine		N ⁺ H ₂ 8.36	R-C(=O)-NH ₂					(21.6)	Cl, H	0.72	
N-Me morpholine	7.38		R= H		(23.5)			(18.9)	HETEROCYCLES		
	-9.3		CH ₃	15.1	(25.5)			(17.2)		(20.95)	
DABCO		2.97, 8.82 (2.97, 8.93)	Ph		(23.3)	PhSO ₂ NHNH ₂		(17.2)		NH	(23.0)
	6.90, 9.95		CF ₃		(17.2)	PhNHNHPh		(26.1)		NH	(18.6)
Proton Sponge		-9.0, 12.0 (--, 7.50)	NH ₂ (urea)		(26.9)	HYDROXAMIC ACID			1,2,3 triazole		
PhCN ⁺ H	-10		OEt		(24.8)			8.88 (NH)		(17.0)	
					(21.6)					NH	(13.9)
					(24.1)						
					12 (20.5)						

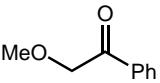
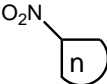
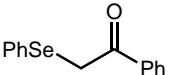
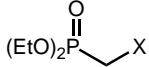
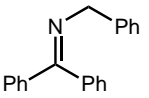
*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

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

*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

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

*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	REFERENCES
ETHERS			PHOSPHONIUM			NITRO			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 ₃ OPh	(49)		P ⁺ H ₄	-14		RNO ₂			
MeOCH ₂ SO ₂ Ph	(30.7)		MeP ⁺ H ₃	2.7		R = CH ₃	≈10	(17.2)	
PhOCH ₂ SO ₂ Ph	(27.9)		Et ₃ P ⁺ H	9.1		CH ₂ Me		(16.7)	
PhOCH ₂ CN	(28.1)		Ph ₃ P ⁺ CH ₃	(22.4)		CHMe ₂		(16.9)	
	(21.1)		Ph ₃ P ⁺ <i>i</i> -Pr	(21.2)		CH ₂ Ph		(12.2)	
SELENIDES			PHOSPONATES & PHOSPHINE OXIDES						
	(18.6)		(EtO) ₂ P(=O)CH ₂ X			n = 3		(26.9)	
PhSeCHPh ₂	(27.5)		X = Ph	(27.6)		4		(17.8)	
(PhSe) ₂ CH ₂	(31.3)		CN	(16.4)		5		(16.0)	
PhSeCH ₂ Ph	(31.0)		CO ₂ Et	(18.6)		6		(17.9)	
PhSeCH=CHCH ₂ SePh	(27.2)		Cl	(26.2)		7		(15.8)	
AMMONIUM						IMINES			
Me ₃ N ⁺ CH ₂ 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 ₂ Ph	(19.4)		PHOSPHINES			Water: Advanced Org. Chem., 3rd Ed. J. March (1985) Unpublished results of W. P. Jencks			
COPh	(14.6)		Ph ₂ PCH ₂ PPh ₂	(29.9)		THF: JACS <u>110</u> , 5705 (1988)			
CO ₂ Et	(20.6)		Ph ₂ PCH ₂ SO ₂ Ph	(20.3)					
CONEt ₂	(24.9)								

*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.