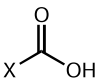
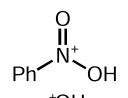
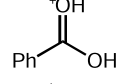
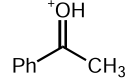
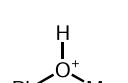
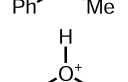
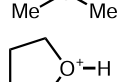
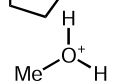
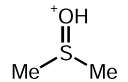
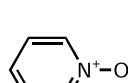
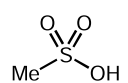
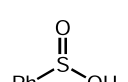
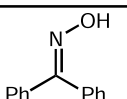
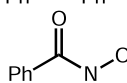
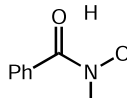
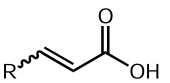
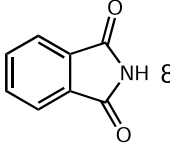
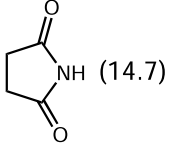
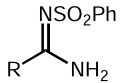
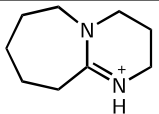
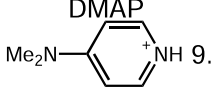
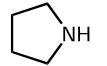
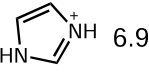
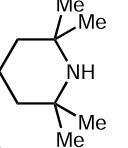
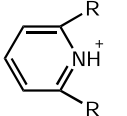
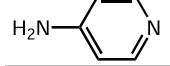
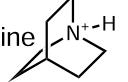
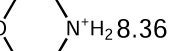
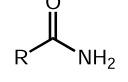
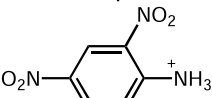
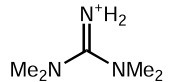
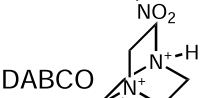
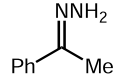
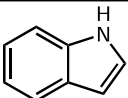
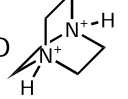
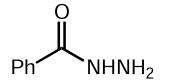
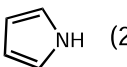
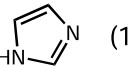
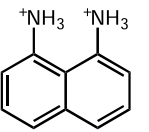
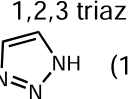
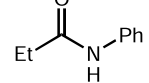
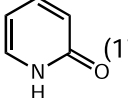
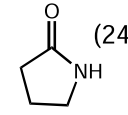
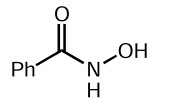
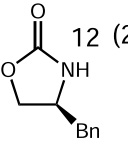
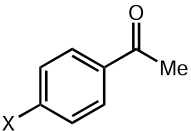
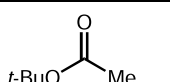
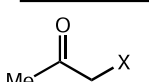
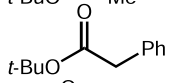
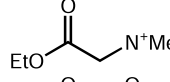
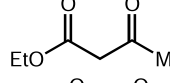

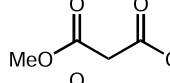
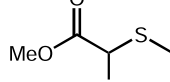
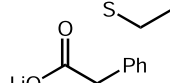
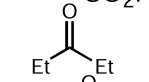

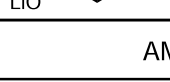
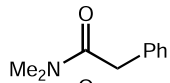
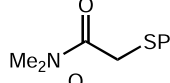
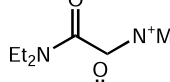
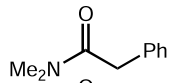
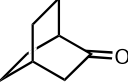
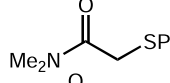
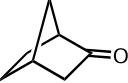
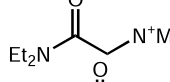
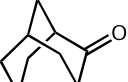
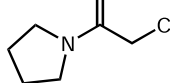
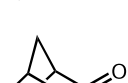
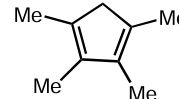
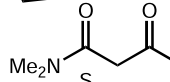
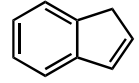
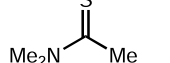



Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O(DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
INORGANIC ACIDS			CARBOXYLIC ACIDS			ALCOHOLS			PROTONATED SPECIES		
H ₂ O	15.7	(32)				HOH	15.7	(31.2)			-12.4
H ₃ O ⁺	-1.7		X= CH ₃	4.76	(12.3)	MeOH	15.54	(27.9)			-7.8
H ₂ S	7.00		CH ₂ NO ₂	1.68		<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
HCIO 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)	SULFINIC & SULFONIC ACIDS		
HSCN	4.00		H	3.77		<i>p</i> -OMeC ₆ H ₄ OH	10.20	(19.1)			-2.6
H ₂ SO ₃	1.9, 7.21		HO	3.6, 10.3		2-naphthol		(17.1)			2.1
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.

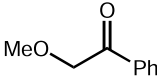
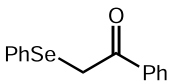
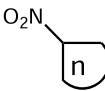
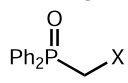
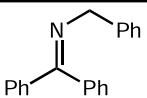
Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
PROTONATED NITROGEN			AMINES			IMIDES			AMIDINES		
N ⁺ H ₄	9.2	(10.5)	HN ₃	4.7	(7.9)		8.30				
EtN ⁺ H ₃	10.6		NH ₃	38	(41)				R= Me	(17.3)	
<i>i</i> -Pr ₂ N ⁺ H ₂	11.05		<i>i</i> -Pr ₂ NH	(36 THF))					R= Ph	(15.0)	
Et ₃ N ⁺ H	10.75	(9.00)	TMS ₂ NH	26(THF)	(30)	Ac ₂ NH		(17.9)			
PhN ⁺ H ₃	4.6	(3.6)	PhNH ₂		(30.6)				PROTONATED HETEROCYCLES		
PhN ⁺ (Me) ₂ H	5.20	(2.50)	Ph ₂ NH		(25.0)	SULFONAMIDE			DBU		(12) (estimate)
Ph ₂ N ⁺ H ₂	0.78		NCNH ₂		(16.9)	MeSO ₂ NH ₂		(17.5)	DMAP		9.2
2-naphthal-N ⁺ H ₃	4.16				(44)	PhSO ₂ NH ₂		(16.1)		6.95	
H ₂ NN ⁺ H ₃	8.12		TMP		(37)	CF ₃ SO ₂ NH ₂	6.3	(9.7)			
HON ⁺ H ₃	5.96				(26.5)	MeSO ₂ NHPh		(12.9)	R= H (PPTS)	5.21	(3.4)
Quinuclidine		11.0	AMIDES & CARBAMATES						R= <i>t</i> -Bu	4.95	(0.90)
Morpholine		8.36							R= Me	6.75	(4.46)
N-Me morpholine	7.38		R= H		(23.5)				R= Cl, H	0.72	
	-9.3		CH ₃	15.1	(25.5)			(13.6)	HETEROCYCLES		
			Ph		(23.3)			(21.6)		(20.95)	
DABCO		2.97, 8.82 (2.97, 8.93)	CF ₃		(17.2)			(18.9)		(23.0)	
H ₃ N ⁺ CH ₂ CH ₂ NH ₃ ⁺	6.90, 9.95		NH ₂ (urea)		(26.9)	PhSO ₂ NHNH ₂		(17.2)		(18.6)	
Proton Sponge		-9.0, 12.0 (--, 7.50)	OEt		(24.8)	PhNHNHPh		(26.1)		1,2,3 triazole	
PhCN ⁺ H	-10				(21.6)	HYDROXAMIC ACID				(17.0)	
				(24.1)			8.88 (NH)	(13.7)			
				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			KETONES						
(Me) ₃ CH	53			24.5	(30.3)				X=			
(Me) ₂ CH ₂	51				(23.6)	X= H		(26.5)	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					COCH ₃	9	(13.3)	Br		(23.8)	
CH ₂ =CHCH ₃	43	(44)		11	(14.2)	SO ₂ Ph		(15.1)	CN		(22.0)	
PhH	43							19-20 (27.1)				
PhCH ₃	41	(43)		13	(15.7)	<i>i</i> -Pr		(28.3)	n=	4	(25.1)	
Ph ₂ CH ₂	33.5	(32.2)			(20.9)	<i>t</i> -Bu		(27.7)	5		(25.8)	
Ph ₃ CH	31.5	(30.6)				Ph		(26.3)	6		(26.4)	
HCCH	24				[30.2 (THF)]	<i>i</i> -Pr			7		(27.7)	
PhCCH	23	(28.8)	AMIDES			X=		(24.7)	8		(27.4)	
XC ₆ H ₄ CH ₃					(26.6)	H		(24.7)				(28.1)
X= <i>p</i> -CN		(30.8)			(25.9)	CH ₃		(24.4)				(29.0)
<i>p</i> -NO ₂		(20.4)			(24.9)	Ph		(17.7)				(25.5)
<i>p</i> -COPh		(26.9)			(17.2)	COCH ₃		(12.7)				(32.4)
		(26.1)			(18.2)	COPh		(13.3)				
	20	(20.1)			(25.7)	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.

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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			Ph ₃ P ⁺ CH ₂ COPh		(6.2)	CH ₂ Bn		(16.2)	
	(18.6)		Ph ₃ P ⁺ CH ₂ CN		(7.0)	CH ₂ SPh		(11.8)	
PhSeCHPh ₂	(27.5)		PHOSPONATES & PHOSPHINE OXIDES			CH ₂ SO ₂ Ph		(7.1)	
(PhSe) ₂ CH ₂	(31.3)		(EtO) ₂ P(=O)CH ₂ X			CH ₂ COPh		(7.7)	
PhSeCH ₂ Ph	(31.0)		X= Ph		(27.6)				
PhSeCH=CHCH ₂ SePh	(27.2)		CN		(16.4)	n= 3		(26.9)	
AMMONIUM			CO ₂ Et		(18.6)	4		(17.8)	
Me ₃ N ⁺ CH ₂ X			Cl		(26.2)	5		(16.0)	
X= CN	(20.6)		SiMe ₃		(28.8)	6		(17.9)	
SO ₂ Ph	(19.4)					7		(15.8)	
COPh	(14.6)		X= SPh		(24.9)	IMINES			
CO ₂ Et	(20.6)		CN		(16.9)			(24.3)	
CONEt ₂	(24.9)		PHOSPHINES			Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts Streitwieser, JOC 1991, 56, 1989			
			Ph ₂ PCH ₂ PPh ₂		(29.9)				
			Ph ₂ PCH ₂ SO ₂ Ph		(20.3)				
						Water: Advanced Org. Chem., 3rd Ed. J. March (1985) Unpublished results of W. P. Jencks			
						THF: JACS <u>110</u> , 5705 (1988)			

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