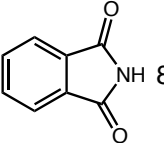
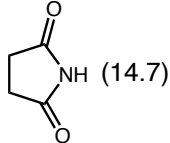
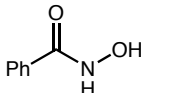
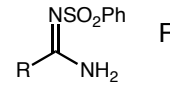
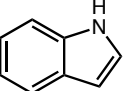
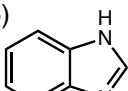
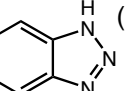
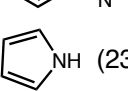
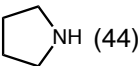
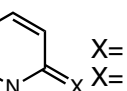
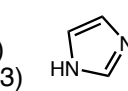
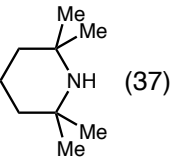
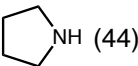
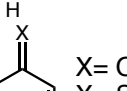
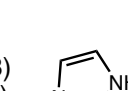
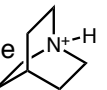
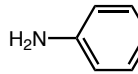
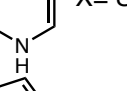
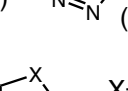
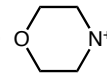
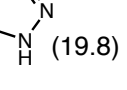
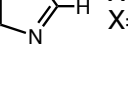
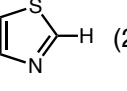
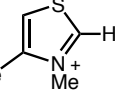
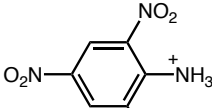
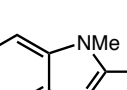
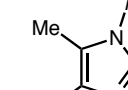
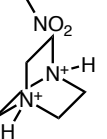
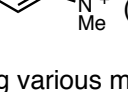
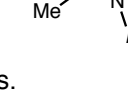
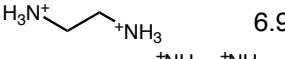


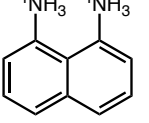
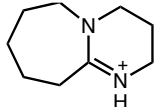


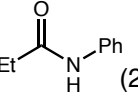
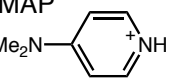
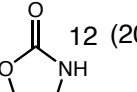
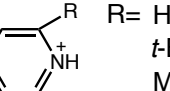
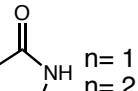
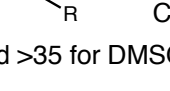
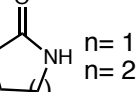

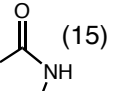
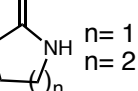


Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O(DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
INORGANIC ACIDS			CARBOXYLIC ACIDS			ALCOHOLS			PROTONATED SPECIES		
H ₂ O	15.7	(32)				HOH	15.7	(31.2)			-12.4
H ₃ O ⁺	-1.7		X= CH ₃	4.76	(12.3)	MeOH	15.5	(27.9)			-7.8
H ₂ S	7.00		CH ₂ NO ₂	1.68		<i>i</i> -PrOH	16.5	(29.3)			-6.2
HBr	-9.00	(0.9)	CH ₂ F	2.66		<i>t</i> -BuOH	17.0	(29.4)			-6.5
HCl	-8.0	(1.8)	CH ₂ Cl	2.86		<i>c</i> -hex ₃ COH	24.0				-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	9.3	(18.2)			-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	8.4				0.79 (+1.63)
HN ₃	4.72	(7.9)	CF ₃	-0.25		<i>p</i> -O ₂ NC ₆ H ₄ OH	7.1	(10.8)			(+5.55)
HSCN	4.00		H	3.77		<i>p</i> -OMeC ₆ H ₄ OH	10.2	(19.1)	SULFINIC & SULFONIC ACIDS		
H ₂ SO ₃	1.9, 7.21		HO	3.6, 10.3		2-naphthol		(17.1)			-2.6
H ₂ SO ₄	-3.0, 1.99		C ₆ H ₅	4.2	(11.1)	OXIMES & HYDROXAMIC ACIDS					2.1
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) (NH)			
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>o</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							

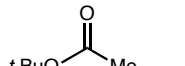
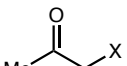
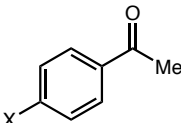
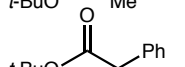
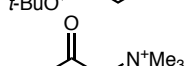
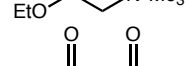

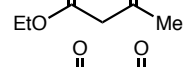
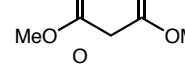
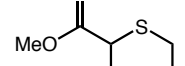
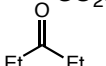

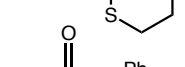
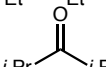
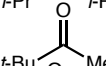
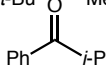
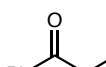
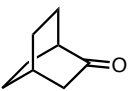
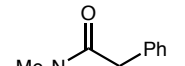
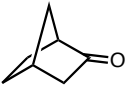
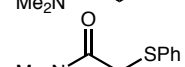
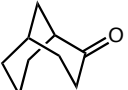
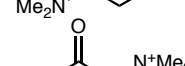
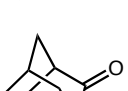
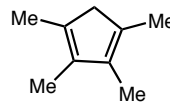
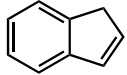
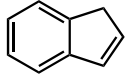


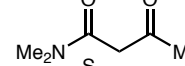
*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: <http://www.chem.wisc.edu/areas/reich/pkatable/index.htm>

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				HYDROXAMIC ACID & 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)		Ac ₂ NH		(17.9)			8.88	(13.7)	
<i>i</i> -Pr ₂ N ⁺ H ₂	11.05			<i>i</i> -Pr ₂ NH	(36 THF))								R= Me	(17.3)	
Et ₃ N ⁺ H	10.75	(9.00)		TMS ₂ NH	26(THF)	(30)						R= Ph	(15.0)		
PhN ⁺ H ₃	4.6	(3.6)		PhNH ₂	(30.6)			SULFONAMIDE				HETEROCYCLES			
PhN ⁺ (Me) ₂ H	5.20	(2.50)		Ph ₂ NH	(25.0)			RSO ₂ NH ₂	R = Me	(17.5)			(20.95)		(16.4)
Ph ₂ N ⁺ H ₂	0.78			NCNH ₂	(16.9)				R = Ph	(16.1)			(11.9)		(23.0)
2-naphthal-N ⁺ H ₃	4.16				(44)			MeSO ₂ NHPh	CF ₃	6.3	(9.7)		X= O (24)		(18.6)
H ₂ NN ⁺ H ₃	8.12				(37)					(12.9)		X= S (13.3)			
HON ⁺ H ₃	5.96				(44)			GUANIDINIUM, HYDRAZONES, -IDES, & -INES					X= O (14.8)		(13.9)
Quinuclidine 	11.0	(9.80)			(26.5)			Me ₂ N=C=N ⁺ H ₂	(13.6)				X= S (11.8)		(13.9)
Morpholine 	8.36			AMIDES & CARBAMATES				Ph=C=NNH ₂	(18.9)				X= O (24.4)		X= S (27.0)
N-Me morpholine	7.38			R= H	(23.5)			Ph=C=NNHPh	(17.2)				X= S (19.8)		(19.8)
	-9.3			R= CH ₃	15.1	(25.5)		PhSO ₂ NHNH ₂	(17.2)				X= O (16.5)		(16.5)
	2.97, 8.82 (2.97, 8.93)			R= Ph	(21.6)			PhNHNHPh	(26.1)				X= S (18.4)		(18.4)
	6.90, 9.95			(urea) NH ₂	(26.9)			PROTONATED HETEROCYCLES					X= O (24.4)		X= S (27.0)
	-9.0, 12.0 (-, 7.50)			OEt	(24.8)			DBU 	(12)	(estimate)			X= O (29.4)		(16.5)
PhCN ⁺ H	-10				(21.6)			DMAP 	9.2				X= S (29.4)		(16.5)
					12	(20.5)			R= H (PPTS)	5.21	(3.4)		X= O (24.4)		X= S (27.0)
					n= 1	(24.1)			<i>t</i> -Bu	4.95	(0.90)		X= S (18.4)		(18.4)
					n= 2	(26.4)			Me	6.75	(4.46)		X= O (24.4)		(24)
					(15)			Cl, H	0.72				X= S (18.4)		(18.4)
					(20.8)								X= O (24.4)		X= S (27.0)

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

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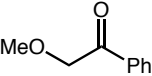
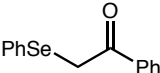
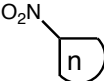
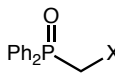
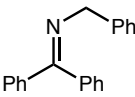
Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
HYDROCARBONS			ESTERS			KETONES					
(Me) ₃ CH	53			24.5	(30.3)						
(Me) ₂ CH ₂	51				(23.6)	X= H		(26.5)	X= H		(24.7)
CH ₂ =CH ₂	50				(20.0)	Ph		(19.8)	OMe		(25.7)
CH ₄	48	(56)			(20.0)	SPh		(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		(12.5)	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)						(27.7)	5		(25.8)
Ph ₃ CH	31.5	(30.6)						(26.3)	6		(26.4)
HCCH	24								7		(27.7)
PhCCH	23	(28.8)				X= H		(24.7)	8		(27.4)
XC ₆ H ₄ CH ₃			AMIDES			CH ₃		(24.4)			(28.1)
X= <i>p</i> -CN		(30.8)			(26.6)	Ph		(17.7)			(29.0)
<i>p</i> -NO ₂		(20.4)			(25.9)	COCH ₃		(14.2)			(25.5)
<i>p</i> -COPh		(26.9)			(24.9)	COPh		(13.3)			
		(26.1)			(17.2)	CN		(10.2)			
	20	(20.1)			(18.2)	F		(21.6)			
	15	(18.0)			(25.7)	OMe		(22.85)			
H ₂	~36					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.

For a comprehensive compilation of Bordwell pKa data see: <http://www.chem.wisc.edu/areas/reich/pkatable/index.htm>

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	(29.0)		<i>t</i> -Bu	(31.2)	
COPh	(10.2)		COPh	(16.9)					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	(20.5)		SOPh	(18.2)		CCH	(22.1)	
OPh	(28.1)		SO ₂ CF ₃	(11.0)			(24.5)		CCPh	(17.8)	
N ⁺ Me ₃	(20.6)		POPh ₂	(24.9)		SULFONIUM			COPh	(11.4)	
SPh	(20.8)		MeSCH ₂ SO ₂ Ph	(23.4)		Me ₃ S ⁺ =O	(18.2)		COMe	(12.5)	
SO ₂ Ph	(12.0)		PhSCHPh ₂	(26.7)			(16.3)		OPh	(27.9)	
HETERO-AROMATICS			(PhS) ₃ CH	(22.8)		SULFIMIDES & SULFOXIMINES			N ⁺ Me ₃	(19.4)	
	(28.2)		(PrS) ₃ CH	(31.3)					CN	(12.0)	
	(30.1)			(23.0)		R= Me	(27.6)		NO ₂	(7.1)	
	(26.7)			(30.5)		<i>i</i> -Pr	(30.7)		SMe	(23.5)	
	(25.2)		X= Ph	(30.7)		Ph	(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				(14.4)			(22.3)	
			R= Me	(24.3)			(20.7)			(31.1)	
			Et	(24.0)						(18.8)	
			<i>i</i> -Pr	(23.6)						(21.8)	
			<i>t</i> -Bu	(22.9)						(26.6)	
			PhSCH=CHCH ₂ SPh	(26.3)						(26.6)	
			BuSH	10-11	(17.0)					(32.8)	
			PhSH	≈7	(10.3)				(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)	
		(22.85)	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)	PHOSPHONATES & PHOSPHINE OXIDES						
(PhSe) ₂ CH ₂		(31.3)	(EtO) ₂ P(=O)CH ₂ X			n= 3		(26.9)	
PhSeCH ₂ Ph		(31.0)	X= Ph		(27.6)	4		(17.8)	
PhSeCH=CHCH ₂ SePh		(27.2)	CN		(16.4)	5		(16.0)	
AMMONIUM			CO ₂ Et		(18.6)	6		(17.9)	
Me ₃ N ⁺ CH ₂ X			Cl		(26.2)	7		(15.8)	
X= CN		(20.6)	SiMe ₃		(28.8)	IMINES			
SO ₂ Ph		(19.4)						(24.3)	
COPh		(14.6)	X= SPh		(24.9)	Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts Streitwieser, JOC 1991, 56, 1989			
CO ₂ Et		(20.0)	CN		(16.9)				
CONEt ₂		(24.9)	PHOSPHINES						
			Ph ₂ PCH ₂ PPh ₂		(29.9)				
			Ph ₂ PCH ₂ SO ₂ Ph		(20.2)				

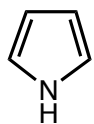
*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: <http://www.chem.wisc.edu/areas/reich/pkatable/index.htm>

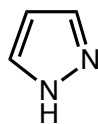
DMSO Acidities of Common Heterocycles

Bordwell, ACR, 1988, 21, 456

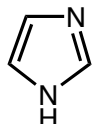
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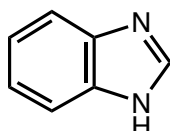
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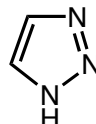
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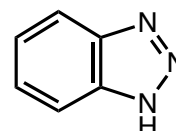
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16.4



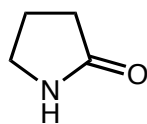
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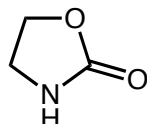
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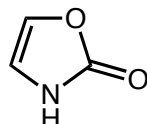
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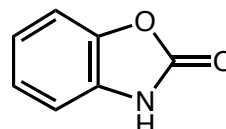
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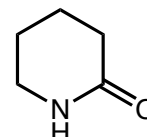
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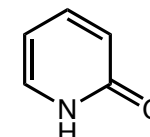
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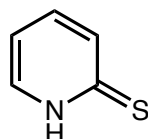
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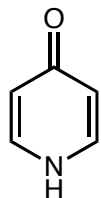
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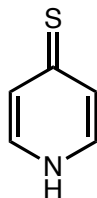
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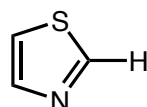
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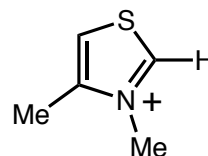
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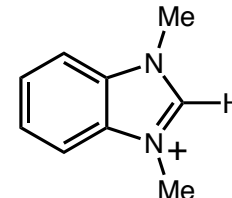
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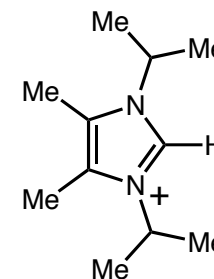
29.4



16.5



18.4



24