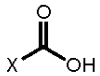
D.H. Ripin, D.A. Evans

pKa's of Inorganic and Oxo-Acids

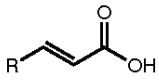
INORGANIC ACIDS

Substrate	pKa H_2O	(DMSO)
H_2O	14.0	(32)
H_3O^+	0.0	
H_2S	7.00	
HBr	-9.00	(0.9)
HCl	-8.0	(1.8)
HF	3.17	(15)
HOCl	7.5	
$HClO_4$	-10	
HCN	9.4	(12.9)
HN_3	4.72	(7.9)
HSCN	4.00	
H_2SO_3	1.9, 7.21	
H_2SO_4	-3.0, 1.99	
H_3PO_4	2.12, 7.21, 12.32	
HNO_3	-1.3	
HNO_2	3.29	
H_2CrO_4	-0.98, 6.50	
CH_3SO_3H	-2.6	(1.6)
CF_3SO_3H	-14	(0.3)
NH_4Cl	9.24	
$B(OH)_3$	9.23	
HOOH	11.6	

CARBOXYLIC ACIDS



X=	pKa H_2O	(DMSO)
CH_3	4.76	(12.3)
CH_2NO_2	1.68	
CH_2F	2.66	
CH_2Cl	2.86	
CH_2Br	2.86	
CH_2I	3.12	
$CHCl_2$	1.29	
CCl_3	0.65	
CF_3	-0.25	
H	3.77	
HO	3.6, 10.3	
C_6H_5	4.2	(11.1)
o-$O_2NC_6H_4$	2.17	
m-$O_2NC_6H_4$	2.45	
p-$O_2NC_6H_4$	3.44	
o-ClC_6H_4	2.94	
m-ClC_6H_4	3.83	
p-ClC_6H_4	3.99	
o-$(CH_3)_3N^+C_6H_4$	1.37	
p-$(CH_3)_3N^+C_6H_4$	3.43	
p-$OMeC_6H_4$	4.47	

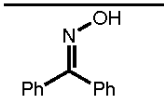


R=	pKa H_2O	(DMSO)
H	4.25	
trans-CO_2H	3.02, 4.38	
cis-CO_2H	1.92, 6.23	

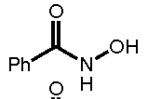
ALCOHOLS

	pKa H_2O	(DMSO)
HOH	14.0	(31.2)
MeOH	15.5	(27.9)
i-PrOH	16.5	(29.3)
t-BuOH	17.0	(29.4)
c-hex_3COH	24.0	
CF_3CH_2OH	12.5	(23.5)
$(CF_3)_2CHOH$	9.3	(18.2)
C_6H_5OH	9.95	(18.0)
m-$O_2NC_6H_4OH$	8.4	
p-$O_2NC_6H_4OH$	7.1	(10.8)
p-$OMeC_6H_4OH$	10.2	(19.1)
2-napthol		(17.1)

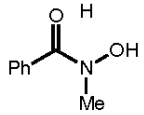
OXIMES & HYDROXAMIC ACIDS



pKa H_2O	(DMSO)
11.3	(20.1)



pKa H_2O	(DMSO)
8.88 (NH)	(13.7)

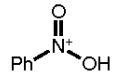


pKa H_2O	(DMSO)
	(18.5)

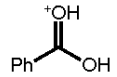
PEROXIDES

	pKa H_2O
MeOOH	11.5
CH_3CO_3H	8.2

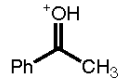
PROTONATED SPECIES



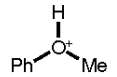
pKa H_2O
-12.4



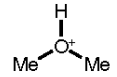
pKa H_2O
-7.8



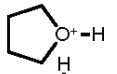
pKa H_2O
-6.2



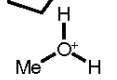
pKa H_2O
-6.5



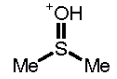
pKa H_2O
-3.8



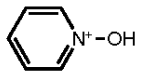
pKa H_2O
-2.05



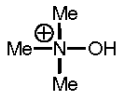
pKa H_2O
-2.2



pKa H_2O
-1.8

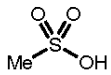


pKa H_2O	(DMSO)
0.79	(+1.63)

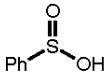


pKa H_2O	(DMSO)
	(+5.55)

SULFINIC & SULFONIC ACIDS



pKa H_2O
-2.6



pKa H_2O
2.1

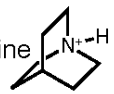
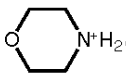
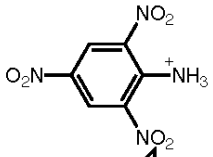
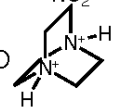
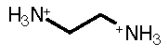
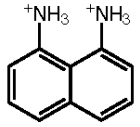
*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

The pka of water and H_3O^+ have been experimentally determined to be 14.0 and 0.0, respectively. Earlier values of 15.7 and –1.74, respectively are erroneous numbers proposed by scientists who made some errors in the calculated "rational" values. See: 1) *Helv. Chim. Acta* **2014**, *97*, 1. and 2) *J. Chem. Educ.* **2017**, *94*, 690.

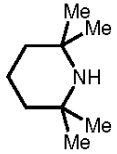
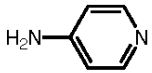
D.H. Ripin, D.A. Evans

pKa's of Nitrogen Acids

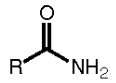
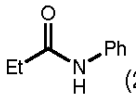
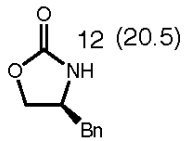
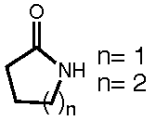
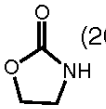
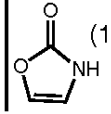
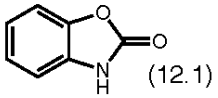
PROTONATED NITROGEN

Substrate	pKa H_2O	(DMSO)
N^+H_4	9.2	(10.5)
EtN^+H_3	10.6	
$i\text{-}Pr_2N^+H_2$	11.05	
Et_3N^+H	10.75	(9.00)
PhN^+H_3	4.6	(3.6)
$PhN^+(Me)_2H$	5.20	(2.50)
$Ph_2N^+H_2$	0.78	
2-napthal-N^+H_3	4.16	
$H_2NN^+H_3$	8.12	
HON^+H_3	5.96	
Quinuclidine 	11.0	(9.80)
Morpholine 	8.36	
N-Me morpholine	7.38	
	-9.3	
DABCO 	2.97, 8.82 (2.97, 8.93)	
	6.90, 9.95	
Proton Sponge 	-9.0, 12.0 (--, 7.50)	
$PhCN^+H$	-10	

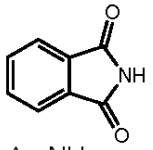
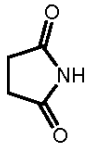
AMINES

HN_3	4.7	(7.9)
NH_3	38	(41)
$i\text{-}Pr_2NH$	(36 THF))	
TMS_2NH	26(THF)	(30)
$PhNH_2$	(30.6)	
Ph_2NH	(25.0)	
$NCNH_2$	(16.9)	
	(44)	
	(37)	
	(26.5)	

AMIDES & CARBAMATES

	R=	H	(23.5)
		CH_3 15.1	(25.5)
		Ph	(23.3)
		CF_3	(17.2)
	(urea)	NH_2	(26.9)
		OEt	(24.8)
			(21.6)
		12	(20.5)
	n= 1 (24.1) n= 2 (26.4)		
			(20.8)
			(15)
			(12.1)

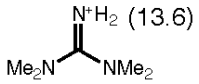
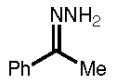
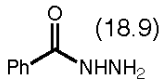
IMIDES

	8.30		(14.7)
Ac_2NH			(17.9)

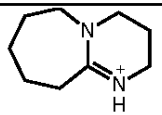
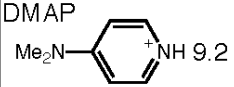
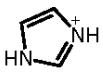
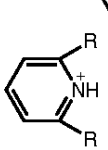
SULFONAMIDE

RSO_2NH_2	R = Me	(17.5)
	Ph	(16.1)
	CF_3 6.3	(9.7)
$MeSO_2NHPh$		(12.9)

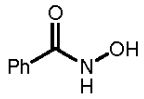
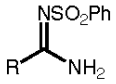
GUANIDINIUM, HYRDAZONES,- IDES, & -INES

	(13.6)		(21.6)
	(18.9)		
$PhSO_2NHNH_2$			(17.2)
PhNHNHPh			(26.1)

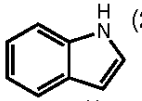
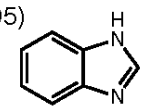
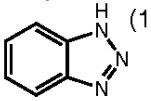
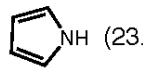
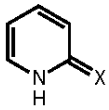
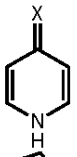
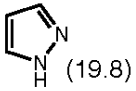
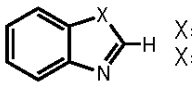
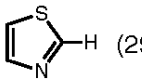
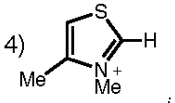
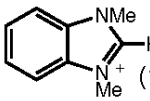
PROTONATED HETEROCYCLES

DBU 			(12) (estimate)
DMAP 	9.2		6.95
	R= H (PPTS)	5.21	(3.4)
	t-Bu	4.95	(0.90)
	Me	6.75	(4.46)
	Cl, H	0.72	

HYDROXAMIC ACID & AMIDINES

		8.88 (NH)	(13.7)
	R= Me		(17.3)
	Ph		(15.0)

HETEROCYCLES

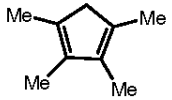
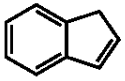
	(20.95)		(16.4)
	(11.9)		(23.0)
	X= O (24) X= S (13.3)		(18.6)
	X= O (14.8) X= S (11.8)		(13.9)
	(19.8)		X= O (24.4) X= S (27.0)
	(29.4)		(16.5)
	(18.4)		(24)

*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

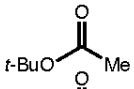
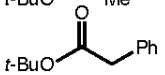
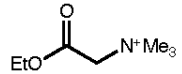
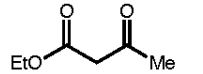
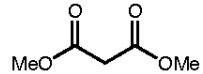
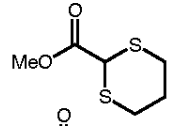
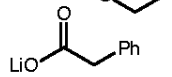
D.H. Ripin, D.A. Evans

pKa's of CH bonds in Hydrocarbons and Carbonyl Compounds

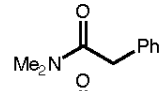
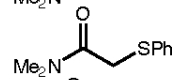
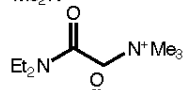
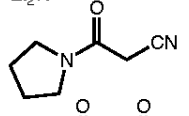
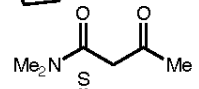
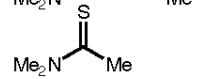
HYDROCARBONS

Substrate	pKa H_2O	(DMSO)
$(Me)_3CH$	53	
$(Me)_2CH_2$	51	
$CH_2=CH_2$	50	
CH_4	48	(56)
△	46	
$CH_2=CHCH_3$	43	(44)
PhH	43	
$PhCH_3$	41	(43)
Ph_2CH_2	33.5	(32.2)
Ph_3CH	31.5	(30.6)
HCCH	24	
PhCCH	23	(28.8)
$XC_6H_4CH_3$		
X= *p*-CN		(30.8)
p-NO_2		(20.4)
p-COPh		(26.9)
		(26.1)
	20	(20.1)
	15	(18.0)
H_2	~36	

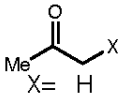
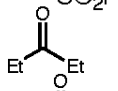
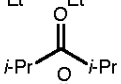
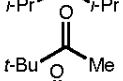
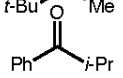
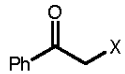
ESTERS

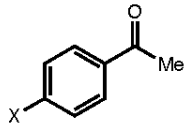
	24.5	(30.3)
		(23.6)
		(20.0)
	11	(14.2)
	13	(15.7)
		(20.9)
		[30.2 (THF)]

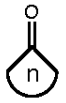
AMIDES

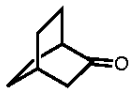
	(26.6)
	(25.9)
	(24.9)
	(17.2)
	(18.2)
	(25.7)

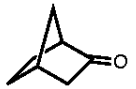
KETONES

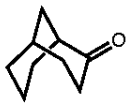
 X=	H	(26.5)
	Ph	(19.8)
	SPh	(18.7)
	$COCH_3$	9 (13.3)
	SO_2Ph	(12.5)
		19-20 (27.1)
		(28.3)
		(27.7)
		(26.3)
 X=	H	(24.7)
	CH_3	(24.4)
	Ph	(17.7)
	$COCH_3$	(14.2)
	COPh	(13.3)
	CN	(10.2)
	F	(21.6)
	OMe	(22.85)
	OPh	(21.1)
	SPh	(16.9)
	SePh	(18.6)
	NPh_2	(20.3)
	N^+Me_3	(14.6)
	NO_2	(7.7)
	SO_2Ph	(11.4)

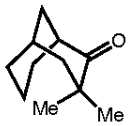

X= H (24.7)
OMe (25.7)
NMe_2 (27.5)
Br (23.8)
CN (22.0)


n= 4 (25.1)
5 (25.8)
6 (26.4)
7 (27.7)
8 (27.4)

 (28.1)

 (29.0)

 (25.5)

 (32.4)

*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

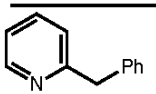
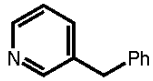
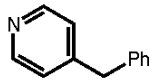
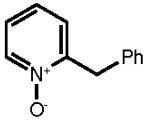
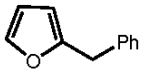
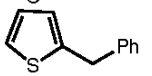
D.H. Ripin, D.A. Evans

pKa's of CH bonds at Nitrile, Heteroaromatic, and Sulfur Substituted Carbon

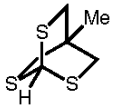
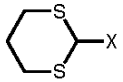
NITRILES

Substrate		pKa H_2O	pKa (DMSO)
			
X=	H		(31.3)
	CH_3		(32.5)
	Ph		(21.9)
	COPh		(10.2)
	$CONR_2$		(17.1)
	CO_2Et		(13.1)
	CN	11	(11.1)
	OPh		(28.1)
	N^+Me_3		(20.6)
	SPh		(20.8)
	SO_2Ph		(12.0)

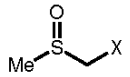
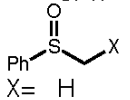
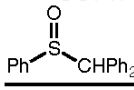
HETERO-AROMATICS

		(28.2)
		(30.1)
		(26.7)
		(25.2)
		(30.2)
		(30.0)

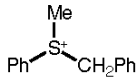
SULFIDES

Substrate		pKa H_2O	pKa (DMSO)
$PhSCH_2X$			
X=	Ph		(30.8)
	CN		(20.8)
	$COCH_3$		(18.7)
	COPh		(16.9)
	NO_2		(11.8)
	SPh		(30.8)
	SO_2Ph		(20.5)
	SO_2CF_3		(11.0)
	$POPh_2$		(24.9)
$MeSCH_2SO_2Ph$			(23.4)
$PhSCHPh_2$			(26.7)
$(PhS)_3CH$			(22.8)
$(PrS)_3CH$			(31.3)
			(30.5)
$(PhS)_2CHPh$			(23.0)
			
X=	Ph		(30.7)
	CO_2Me		(20.8)
	CN		(19.1)
$RSCH_2CN$			
R=	Me		(24.3)
	Et		(24.0)
	i-Pr		(23.6)
	t-Bu		(22.9)
$PhSCH=CHCH_2SPh$			(26.3)
BuSH		10-11	(17.0)
PhSH		≈7	(10.3)

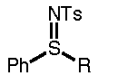
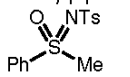
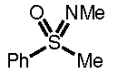
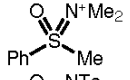
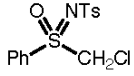
SULFOXIDES

		
X=	H	(35.1)
	Ph	(29.0)
	SPh	(29.0)
		
X=	H	(33)
	Ph	(27.2)
	SOPh	(18.2)
		(24.5)

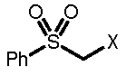
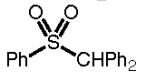
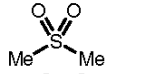
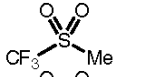
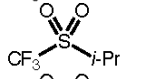
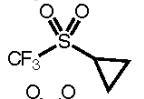
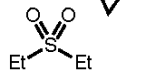
SULFONIUM

$Me_3S^+=O$	(18.2)
	(16.3)

SULFIMIDES & SULFOXIMINES

		
R=	Me	(27.6)
	i-Pr	(30.7)
		(24.5)
		(33)
		(14.4)
		(20.7)

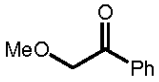
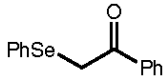
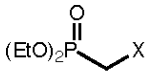
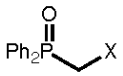
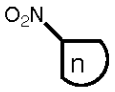
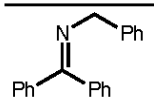
SULFONES

		
X=	H	(29.0)
	CH_3	(31.0)
	t-Bu	(31.2)
	Ph	(23.4)
	$CH=CH_2$	(22.5)
	CH=CHPh	(20.2)
	CCH	
	CCPh	(22.1)
	COPh	(11.4)
	COMe	(12.5)
	OPh	(27.9)
	N^+Me_3	(19.4)
	CN	(12.0)
	NO_2	(7.1)
	SMe	(23.5)
	SPh	(20.5)
	SO_2Ph	(12.2)
	PPh_2	(20.2)
		(22.3)
		(31.1)
		(18.8)
		(21.8)
		(26.6)
		(32.8)
$(PhSO_2)_2CH_2Me$		(14.3)

*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

D. H. Ripin, D. A. Evans

pKa's of CH bonds at Heteroatom Substituted Carbon & References

Substrate	pKa H_2O	(DMSO)
ETHERS		
CH_3OPh		(49)
$MeOCH_2SO_2Ph$		(30.7)
$PhOCH_2SO_2Ph$		(27.9)
$PhOCH_2CN$		(28.1)
		(22.85)
SELENIDES		
		(18.6)
$PhSeCHPh_2$		(27.5)
$(PhSe)_2CH_2$		(31.3)
$PhSeCH_2Ph$		(31.0)
$PhSeCH{=}CHCH_2SePh$		(27.2)
AMMONIUM		
$Me_3N^+CH_2X$		
X= CN		(20.6)
SO_2Ph		(19.4)
COPh		(14.6)
CO_2Et		(20.0)
$CONEt_2$		(24.9)
PHOSPHONIUM		
P^+H_4		-14
MeP^+H_3		2.7
Et_3P^+H		9.1
$Ph_3P^+CH_3$		(22.4)
$Ph_3P^+i\text{-}Pr$		(21.2)
$Ph_3P^+CH_2COPh$		(6.2)
$Ph_3P^+CH_2CN$		(7.0)
PHOSPONATES & PHOSPHINE OXIDES		
		
X= Ph		(27.6)
CN		(16.4)
CO_2Et		(18.6)
Cl		(26.2)
$SiMe_3$		(28.8)
		
X= SPh		(24.9)
CN		(16.9)
PHOSPHINES		
$Ph_2PCH_2PPh_2$		(29.9)
$Ph_2PCH_2SO_2Ph$		(20.2)
NITRO		
RNO_2		
R= CH_3	≈10	(17.2)
CH_2Me		(16.7)
$CHMe_2$		(16.9)
CH_2Ph		(12.2)
CH_2Bn		(16.2)
CH_2SPh		(11.8)
CH_2SO_2Ph		(7.1)
CH_2COPh		(7.7)
		
n= 3		(26.9)
4		(17.8)
5		(16.0)
6		(17.9)
7		(15.8)
IMINES		
		(24.3)

Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts
Streitwieser, JOC 1991, 56, 1989

REFERENCES

DMSO:

JACS 97, 7007 (1975)
JACS 97, 7160 (1975)
JACS 97, 442 (1975)
JACS 105, 6188 (1983)
JOC 41, 1883 (1976)
JOC 41, 1885 (1976)
JOC 41, 2786 (1976)
JOC 41, 2508 (1976)
JOC 42, 1817 (1977)
JOC 42, 321 (1977)
JOC 42, 326 (1977)
JOC 43, 3113 (1978)
JOC 43, 3095 (1978)
JOC 43, 1764 (1978)
JOC 45, 3325 (1980)
JOC 45, 3305 (1980)
JOC 45, 3884 (1980)
JOC 46, 4327 (1981)
JOC 46, 632 (1981)
JOC 47, 3224 (1982)
JOC 47, 2504 (1982)
Acc. Chem. Res. 21, 456 (1988)
Unpublished results of F. Bordwell

Water:

Advanced Org. Chem., 3rd Ed.
J. March (1985)
Unpublished results of W. P. Jencks

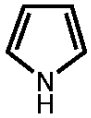
THF:
JACS 110, 5705 (1988)

See cited website below for additional data

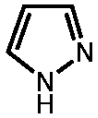
*Values <0 for H_2O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

DMSO Acidities of Common Heterocycles

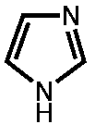
Bordwell, ACR, **1988**, *21*, 456
Bordwell http://www.chem.wisc.edu/areas/reich/pkatable/index.htm



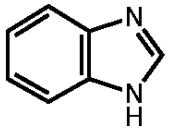
23.0



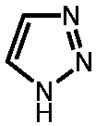
19.8



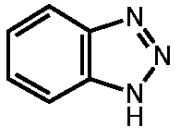
18.6



16.4

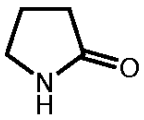


13.9

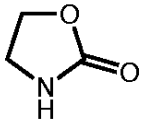


11.9

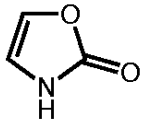
18.0



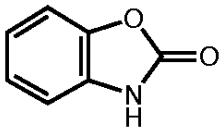
24.0



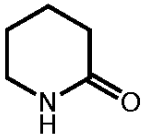
20.8



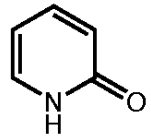
15.0



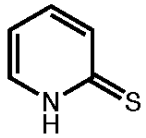
12.1



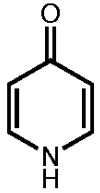
26.4



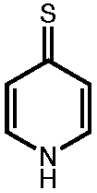
24.0



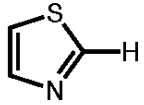
13.3



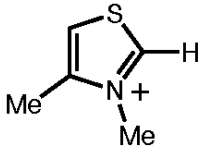
14.8



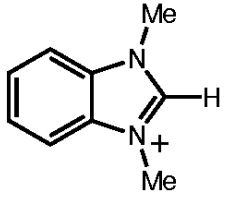
11.8



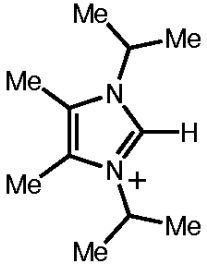
29.4



16.5



18.4



24