Substrate	pKa H ₂ O (DMSO)	Substrate pKa	H ₂ O(DMSO)	Substrate	pKa H ₂ O (DMSO)	Substrate	pKa H ₂ O (DMSO)		
INORG	ANIC ACIDS	CARBOXYLIC	ACIDS	ALC	COHOLS	PROTONATED SPECIES			
H ₂ O H ₃ O ⁺	15.7 (32) -1.7	X OH		HOH MeOH	15.7 (31.2) 15.54 (27.9)	0	-12.4		
H ₂ S HBr	7.00 -9.00 (0.9)	$X = CH_3$ CH_2NO_2	4.76 (12.3) 1.68	<i>i</i> -PrOH <i>t</i> -BuOH	16.5 (29.3) 17 (29.4)	Ph OH +OH	-12.4		
НСІ	-8.0 (1.8)	CH ₂ F CH ₂ Cl CH ₂ Br	2.66 2.86 2.86	c-hex₃COH	24	Ph OH OH II			
HF HOCI	3.17 (15) 7.5	СН ₂ I СНСІ ₂	3.12 1.29	CF ₃ CH ₂ OH (CF ₃) ₂ CHOH		Ph CH ₃	-6.2		
HCIO ₄	-10	CCl ₃ CF ₃	0.65 -0.25	C ₆ H ₅ OH <i>m</i> -O ₂ NC ₆ H ₄ C	9.95 (18.0) OH 8.35	Ph Me	-6.5		
HCN HN ₃	9.4 (12.9) 4.72 (7.9)	H HO	3.77 3.6, 10.3	<i>p</i> -O ₂ NC ₆ H ₄ O <i>p</i> -OMeC ₆ H ₄ O		H I O ⁺ Me	-3.8		
HSCN	4.00	C ₆ H ₅ <i>o</i> -O ₂ NC ₆ H ₄	4.2 (11.1) 2.17	2-napthol	(17.1)	Ĥ O₊–H	-2.05		
H_2SO_3 H_2SO_4	1.9, 7.21 -3.0, 1.99	<i>m</i> -O ₂ NC ₆ H ₄ <i>p</i> -O ₂ NC ₆ H ₄	2.45 3.44	OXIMES & HY	DROXAMIC ACIDS	Me O ⁺OH	-2.2		
H ₃ PO ₄	2.12, 7.21, 12.32	o-CIC ₆ H₄ m-CIC ₆ H₄	2.94 3.83	Ph Ph	11.3 (20.1)	Me Me	-1.8		
HNO_3 HNO_2	-1.3 3.29	<i>p</i> -CIC ₆ H ₄ <i>o</i> -(CH ₃) ₃ N ⁺ C ₆ F	3.99	Ph N OH	8.88 (13.7) (NH)	N⁺-OH	0.79		
H ₂ CrO ₄	-0.98, 6.50	<i>p</i> -(CH ₃) ₃ N ⁺ C ₆ I <i>p</i> -OMeC ₆ H ₄		Ph N OH Me	(18.5)	SULFINIC & S	SULFONIC ACIDS		
CH ₃ SO ₃ H CF ₃ SO ₃ H	-2.6 (1.6) -14 (0.3)	RMOH		PER	OXIDES	O O V// Me/S OH	-2.6		
NH ₄ CI B(OH) ₃	9.24 9.23	R= H trans-CO ₂ H	4.25 3.02, 4.38	MeOOH	11.5 8.2	0 S	2.1		
НООН	11.6	cis-CO ₂ H	1.92, 6.23	CH₃CO₃H	0.2	Ph OH			

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

Substrate p	Ka H ₂ O ((DMSO)) Substrate pk	(a H ₂ O	(DMSO)	Substrate	pKa H ₂ O	(DMSO)	Substrate	pKa H ₂ O (DMSO)	
PROTONATE	D NITROGE	AMI	NES		[IMIDES		AMIDINES			
N ⁺ H ₄ EtN ⁺ H ₃	10.6	(10.5)	HN ₃ NH ₃ <i>i</i> -Pr ₂ NH	4.7 38 (36 THF))	(7.9) (41)	NH	8.30 NI	н (14.7)	R = Me	(17.3)	
<i>i</i> -Pr ₂ N ⁺ H ₂	11.05		_	26(THF)	(30)		S.50	(, , , ,	R= Me Ph	(17.3)	
Et ₃ N ⁺ H		(9.00)	PhNH ₂		(30.6)	Ō	Ö		DDOTONATE	ED HETEROCYCLES	
PhN ⁺ H ₃		(3.6)	Ph ₂ NH		(25.0)	Ac ₂ NH		(17.9)	- FROTONATE	.DTIETEROCTCEES	
PhN ⁺ (Me) ₂ H Ph ₂ N ⁺ H ₂	5.20 0.78	(2.50)	NCNH ₂		(16.9) (44)	SUL	FONAMIDE		DBU <	(12) (estimate)	
2-napthal-N ⁺ H ₃	4.16			Me Me		MeSO ₂ NH ₂		(17.5)	DMAP	Н	
$H_2NN^+H_3$	8.12		TMP <	NH	(37)	PhSO ₂ NH ₂		(16.1)		NH 9.2 NH 6.95	
HON⁺H ₃	5.96			Me		CF ₃ SO ₂ NH ₂	6.3	(9.7)	e211	HN 0.33	
Quinuclidine N	TH 11.0	(9.80)	H_2N	Me	(26.5)	MeSO ₂ NHPh		(12.9)	∕=\rightarrow R		
Morpholine o	N⁺H₂8.36		AMIDES & C	ARBAMA	TES		ANIDINIUM, IES,- IDES, &	& -INES	NH [†]		
N-Me morpholine	7.38		$R \longrightarrow NH_2$			Me_2N N^+H_2 NMe_2	2	(13.6)	R= H (PPTS t-Bu	5) 5.21 (3.4) 4.95 (0.90) 6.75 (4.46)	
O ₂ N	l ₃ -9.3		R= H CH ₃ Ph	15.1	(23.5) (25.5) (23.3)	NNH ₂		(21.6)	Me Cl, H	0.72 EROCYCLES	
NO ₂	2.97, 8.	g2	CF ₃ NH ₂ (urea)		(17.2) (26.9)	Ph NHNH ₂		(18.9)	HE IE	H ·N	
DABCO	(2.97, 8	3.93)	OEt		(24.8)	PhSO ₂ NHNH	1_	(17.2)		(20.95)	
H ₃ N ⁺ → +NH ₃ +NH	6.90, 9. ₁₃ +ŅH ₃	.95	Et N Ph		(21.6)	PhNHNHPh		(26.1)	NH (23.	0) N (18.6)	
Proton Sponge	-9.0 (,	0, 12.0 7.50)	(24.1) NH	0 12 NH	(20.5)	HYDRO	DXAMIC ACI			1,2,3 triazole	
PhCN ⁺ H	-10 /alues <0 for	H ₂ O ar	/ nd DMSO, and val	Bn ues >14 fo	or water a	Ph N OH H nd >35 for DMS	8.88 NH) SO were extra)	(17.0 N O N O N O N O N O N O N O N O N O N	N=N	

'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)
HYDR	HYDROCARBONS			ESTERS				KETONES						
(Me) ₃ CH	53		0		24.5	(30.3)	 					M e		
$(Me)_2CH_2$	51		t-BuO Me			` .	Me X			(26.5)	x ·			
CH ₂ =CH ₂	50		t-BuO	Ph		(23.6)	X= H Ph			(19.8)	X= H			(24.7)
CH ₄	48	(56)	<u></u>			(00.0)	SPh COCH₃		9	(18.7) (13.3)	OMe NMe ₂			(25.7) (27.5)
\triangle	46		EtO N	⁺Me ₃		(20.0)	SO ₂ Ph		3	(15.1)	Br _			(23.8) (22.0)
CH ₂ =CHCH ₃	43	(44)			11	(14.2)	ļ Ļ		19-2	0 (27.1)	CN o			(22.0)
PhH	43		EtO O	`Me O			Et Et O			(28.3)	Ļ			
PhCH ₃	41	(43)	MeO	OMe	13	(15.7)	i-Pr Oi-Pr			(20.3)	n			
Ph ₂ CH ₂	33.5	(32.2)	O II	Oivie			t-Bu O Me			(27.7)	n= 4			(25.1)
Ph ₃ CH	31.5	(30.6)	MeO S	§		(20.9)	l Å			(26.3)	5			(25.8)
НССН	24	()	o Ś	/			Ph i-Pr O				6 7			(26.4) (27.7)
PhCCH	23	(28.8)	LiO PI	า	[30.	.2 (THF)]	Ph X				8			(27.4)
XC ₆ H ₄ CH ₃				AMIDE	·S		X= H			(24.7)	1			
X = p - CN		(30.8)	0	711111111111111111111111111111111111111		(20, 0)	CH ₃ Ph			(24.4) (17.7)				(28.1)
<i>p</i> −NO ₂		(20.4)	Me ₂ N	Ph		(26.6)	COCH ₃			(12.7)	\ \ \ \ \			
<i>p</i> -COPh		(26.9)				(25.9)	COPh			(13.3)	> 0			(29.0)
Me	Л е		Me ₂ N	SPh		(20.0)	CO ₂ Et CN			(22.7) (10.2)	/ \			
		(26.1)		I⁺Me₃		(24.9)	F			(21.6)				(25.5)
Me Me			Et ₂ N O				OMe OPh			(22.85) (21.1)	V V			
	20	(20.1)	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	_CN		(17.2)	SPh			(16.9)	٨			
				O.		(40.0)	SePh			(18.6)				(32.4)
	15	(18.0)	Me ₂ N	⊥ Me		(18.2)	NPh ₂ N ⁺ Me ₃			(20.3) (14.6)	V _{Me} X _{Me}			,
H ₂	~36		S			(25.7)	NO ₂			(7.7)	IVIC			
_			Me ₂ N Me			()	SO ₂ Ph			(11.4)				

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

Substrate	pKa	H ₂ O	(DMSO)	Substrate	рКа	H ₂ O	(DMSO)	Substrate	pKa	H ₂ O	(DMSO)	Substrate	рКа	H ₂ O	(DMSO)
	NITRILES			SULFIDES				SULFOXIDES				SULFONES			
X= H CH ₃ Ph COPh CONR CO ₂ Et CN OPh N ⁺ Me ₃ SPh SO ₂ Ph	-	11	(31.3) (32.5) (21.9) (10.2) (17.1) (13.1) (11.1) (28.1) (20.6) (20.8) (12.0)	PhSCH ₂ X X= Ph CN COC COP NO ₂ SPh SO ₂ C POPI MeSCH ₂ SC PhSCHPh ₂	h Ph CF ₃ 1 ₂ D ₂ Ph		(30.8) (20.8) (18.7) (16.9) (11.8) (30.8) (20.3) (11.0) (24.9) (23.4) (26.7) (22.8)		JLFONI		(35.1) (29.0) (29.0) (33) (27.2) (18.2) (24.5)	X= H CH ₃ t-Bu Ph CH=CH CH=CH CCPh COPh COMe OPh N ⁺ Me ₃ CN			(29.0) (31.0) (31.2) (23.4) (22.5) (20.2) (22.1) (17.8) (11.4) (12.5) (27.9) (19.4) (12.0)
HETER	RO-ARC	OMATIO	CS	(PrS) ₃ CH			(31.3)	Me ₃ S ⁺ =O Me I S ⁺			(18.2) (16.3)	NO ₂ SMe SPh			(7.1) (23.5) (20.5)
Pr	1		(28.2)	SH S (PhS) ₂ CHF	Ph		(30.5)	SULFIMIDE:	S & SU	ILFOXIN	/INES	SO ₂ Ph PPh ₂			(12.2) (20.2) (22.3)
N P	h		(30.1)	$\left\langle \begin{array}{c} S \\ S \end{array} \right\rangle X$				NTs II Ph ^S R R= Me			(27.6)	Ph CHPh ₂ O O N Me Me	2		(31.1)
N P	h		(26.7)	X= Ph CO ₂ N CN	Лe		(30.7) (20.8) (19.1)	i-Pr O NTs V/ Ph Me			(27.6) (30.7) (24.5)	CF ₃ Me			(18.8)
Pr	1		(25.2)	RSCH ₂ CN R= Me			(24.3) (24.0)	O NMe S Me			(33)	CF ₃ S <i>i</i> -Pr			(21.8)
O Ph			(30.2)	Et <i>i</i> -Pr <i>t</i> -Bu			(23.6) (22.9)	O $N^{\dagger}Me_{2}$ S Me O NTs			(14.4)	CF ₃ S			(26.6)
Ph			(30.0)	PhSCH=CH BuSH PhSH	HCH ₂ SI	Ph 10-1 ≈7	(26.3) 1 (17.0) (10.3)	O NTs Ph S CH ₂ CI			(20.7)	$_{\rm Et}$ $^{\rm S}$ $_{\rm Et}$ $_{\rm PhSO_2)_2Cl}$	H 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 pk	Ka H ₂ O	(DMSO)	Substrate	pKa	H ₂ O	(DMSO)	Substrate	pKa	H ₂ O	(DMSO)	REFERENCES
ETHERS			PHOSPHONIUM					NITRO)		NEI ERENOES
CH ₃ OPh MeOCH ₂ SO ₂ Ph PhOCH ₂ SO ₂ Ph PhOCH ₂ CN MeO Ph		(49) (30.7) (27.9) (28.1) (21.1)	P ⁺ H ₄ MeP ⁺ H ₃ Et ₃ P ⁺ H Ph ₃ P ⁺ CH ₃ Ph ₃ P ⁺ <i>i</i> -Pr Ph ₃ P ⁺ CH ₂ C Ph ₃ P ⁺ CH ₂ C			-14 2.7 9.1 (22.4) (21.2) (6.2) (7.0)	_	Me ⁄Ie ₂ Ph	≈10	(17.2) (16.7) (16.9) (12.2) (16.2) (11.8) (7.1)	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)
SELEI	SELENIDES		PHOSPONATES & PHOSPHINE OXIDES			CH_2	COPh		(7.7)	JOC <u>42</u> , 321 (1977) JOC <u>42</u> , 326 (1977) JOC <u>43</u> , 3113 (1978)	
PhSe Ph		(18.6)	$(EtO)_2$ P X				n)			JOC <u>43</u> , 3095 (1978) JOC <u>43</u> , 1764 (1978) JOC <u>45</u> , 3325 (1980)
PhSeCHPh ₂		(27.5)	X= Ph			(27.6)	n= 3			(26.9)	JOC <u>45</u> , 3305 (1980) JOC <u>45</u> , 3884 (1980)
(PhSe) ₂ CH ₂		(31.3)	CN CO ₂ Et	t		(16.4) (18.6)	4			(17.8)	JOC <u>46</u> , 4327 (1981) JOC <u>46</u> , 632 (1981)
PhSeCH ₂ Ph		(31.0)	CI	-		(26.2)	5			(16.0)	JOC <u>47</u> , 3224 (1982)
PhSeCH=CHCH ₂	₂ SePh	(27.2)	SiMe ₃			(28.8)	6 7			(17.9) (15.8)	JOC <u>47</u> , 2504 (1982) Acc. Chem. Res. <u>21</u> , 456 (1988) Unpublished results of F. Bordwell
AMMC	DNIUM		Ph ₂ P X				IMINE	S		Water:	
$Me_3N^+CH_2X$ $X = CN$ SO_2Ph		(20.6) _ (19.4)	X= SPh CN PH	IOSPHI	INFS	(24.9) (16.9)	Ph		10. 1	(24.3)	Advanced Org. Chem., 3rd Ed. J. March (1985) Unpublished results of W. P. Jencks
COPh		(14.6)				i	acidic tha	hers are ~ ` an their ketc ser, JOC 19	ne cou	nterparts	THF:
CO ₂ Et		(20.6)	Ph ₂ PCH ₂ PF			(29.9)		30.,000.	,, ,,	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	JACS <u>110</u> , 5705 (1988)
CONEt ₂		(24.9)	Ph ₂ PCH ₂ S(O ₂ Ph		(20.3)					

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