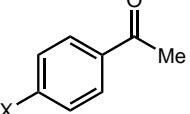
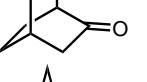
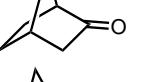
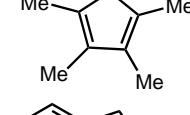
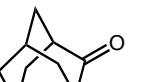
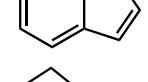


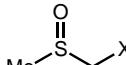
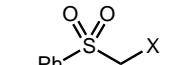
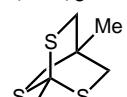
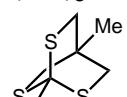
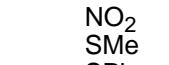
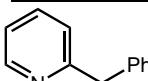
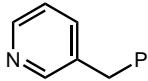
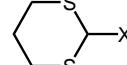
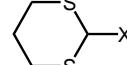
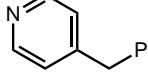
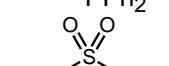
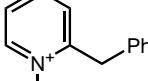
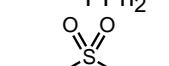
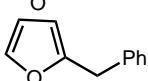
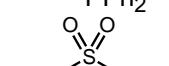
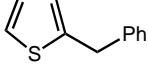
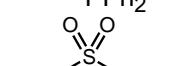
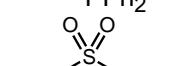
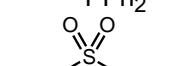
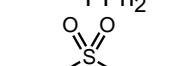
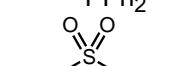
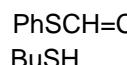
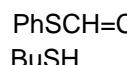
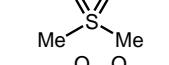
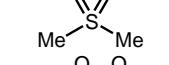
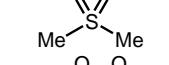
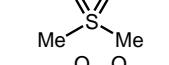
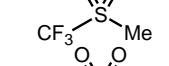
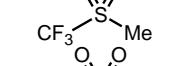
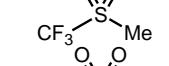
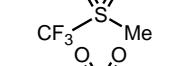
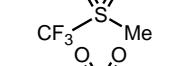
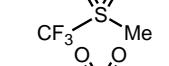
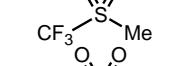
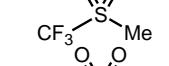
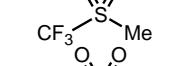
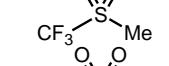
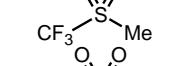
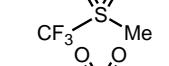
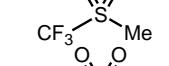
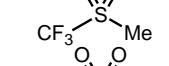
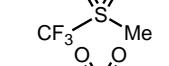
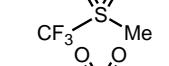
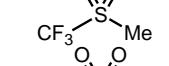
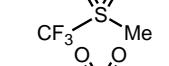
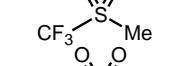
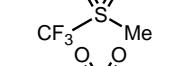
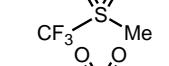
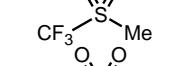
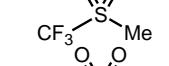
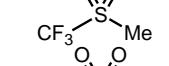
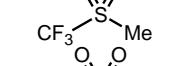
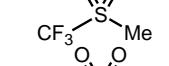
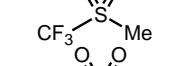
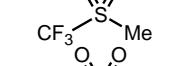
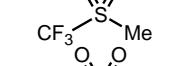
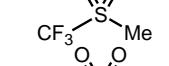
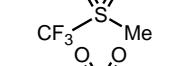
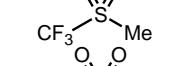
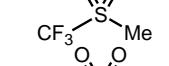
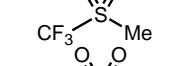
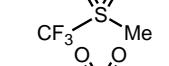
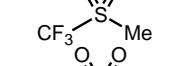
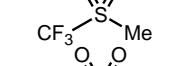
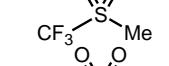
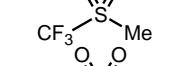
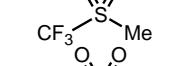
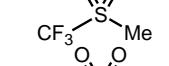
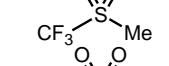
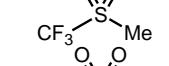
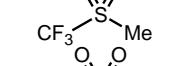
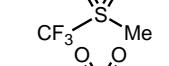
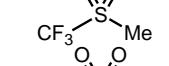
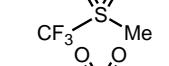
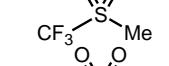
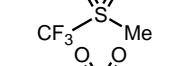
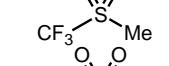
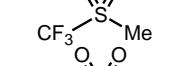
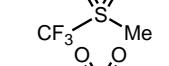
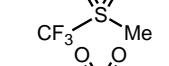
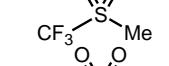
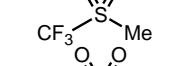
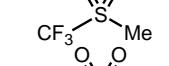
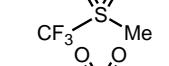
Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)
<b>INORGANIC ACIDS</b>														
<b>CARBOXYLIC ACIDS</b>														
H <sub>2</sub> O	15.7	(32)				4.76 (12.3)	HOH	15.7	(31.2)				-12.4	
H <sub>3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

\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

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Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)				
HYDROCARBONS																			
ESTERS																			
(Me) <sub>3</sub> CH	53			t-BuO-C(=O)Me	24.5	(30.3)		Me-C(=O)X											
(Me) <sub>2</sub> CH <sub>2</sub>	51			t-BuO-C(=O)CH <sub>2</sub> Ph		(23.6)		X= H				X= H			(24.7)				
CH <sub>2</sub> =CH <sub>2</sub>	50			EtO-C(=O)CH <sub>2</sub> N <sup>+</sup> Me <sub>3</sub>		(20.0)		Ph				OMe			(25.7)				
CH <sub>4</sub>	48	(56)		EtO-C(=O)CH <sub>2</sub> C(=O)Me	11	(14.2)		SPh				NMe <sub>2</sub>			(27.5)				
△	46			MeO-C(=O)CH <sub>2</sub> COMe	13	(15.7)		COCH <sub>3</sub>	9	(13.3)		Br			(23.8)				
CH <sub>2</sub> =CHCH <sub>3</sub>	43	(44)		MeO-C(=O)CH <sub>2</sub> CH <sub>2</sub> S		(20.9)		SO <sub>2</sub> Ph		(15.1)		CN			(22.0)				
PhH	43			LiO-C(=O)CH <sub>2</sub> Ph		[30.2 (THF)]													
PhCH <sub>3</sub>	41	(43)										n= 4			(25.1)				
Ph <sub>2</sub> CH <sub>2</sub>	33.5	(32.2)										5			(25.8)				
Ph <sub>3</sub> CH	31.5	(30.6)										6			(26.4)				
HCCH	24											7			(27.7)				
PhCCH	23	(28.8)										8			(27.4)				
XC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>				AMIDES															
X= p-CN			(30.8)															(28.1)	
p-NO <sub>2</sub>			(20.4)															(29.0)	
p-COPh			(26.9)															(25.5)	
			(26.1)															(32.4)	
	20	(20.1)																	
	15	(18.0)																	
H <sub>2</sub>			~36																

\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)
NITRILES				SULFIDES				SULFOXIDES				SULFONES			
NC—X				PhSCH <sub>2</sub> X											
X= H			(31.3)	X= Ph			(30.8)	X= H			(35.1)	X= H			(29.0)
CH <sub>3</sub>			(32.5)	CN			(20.8)	Ph			(29.0)	CH <sub>3</sub>			(31.0)
Ph			(21.9)	COCH <sub>3</sub>			(18.7)	SPh			(29.0)	t-Bu			(31.2)
COPh			(10.2)	COPh			(16.9)	NO <sub>2</sub>			(11.8)	Ph			(23.4)
CONR <sub>2</sub>			(17.1)	SPh			(30.8)	SO <sub>2</sub> Ph			(20.3)	CH=CH <sub>2</sub>			(22.5)
CO <sub>2</sub> Et			(13.1)	SO <sub>2</sub> CF <sub>3</sub>			(11.0)	SO <sub>2</sub> CF <sub>3</sub>			(24.9)	CH=CHPh			(20.2)
CN	11		(11.1)	POPh <sub>2</sub>				POPh <sub>2</sub>				CCH			(22.1)
OPh			(28.1)	MeSCH <sub>2</sub> SO <sub>2</sub> Ph			(23.4)	MeSCH <sub>2</sub> SO <sub>2</sub> Ph			(24.5)	CCPh			(17.8)
N <sup>+</sup> Me <sub>3</sub>			(20.6)	PhSCHPh <sub>2</sub>			(26.7)	PhSCHPh <sub>2</sub>				COPh			(11.4)
SPh			(20.8)	(PhS) <sub>3</sub> CH			(22.8)	(PhS) <sub>3</sub> CH				COMe			(12.5)
SO <sub>2</sub> Ph			(12.0)	(PrS) <sub>3</sub> CH			(31.3)	(PrS) <sub>3</sub> CH				OPh			(27.9)
HETERO-AROMATICS							(30.5)								
			(28.2)	(PhS) <sub>2</sub> CHPh			(23.0)	(PhS) <sub>2</sub> CHPh				Me <sub>3</sub> S <sup>+</sup> O			(18.2)
			(30.1)									Me <sub>3</sub> S <sup>+</sup> O			(16.3)
			(26.7)	X= Ph			(30.7)	X= Ph							
			(25.2)	CO <sub>2</sub> Me			(20.8)	CO <sub>2</sub> Me							
			(30.2)	CN			(19.1)	CN							
			(30.0)	RSCH <sub>2</sub> CN				RSCH <sub>2</sub> CN							
				R= Me			(24.3)	R= Me							
				Et			(24.0)	Et							
				i-Pr			(23.6)	i-Pr							
				t-Bu			(22.9)	t-Bu							
							(26.3)								
				BuSH			10-11	BuSH							
				PhSH			≈7	PhSH							
							(17.0)								
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
															
												<img alt="Chemical structure of a sulfimide: PhS(=O)(CH<sub>2</sub			

Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	REFERENCES
<b>ETHERS</b>				<b>PHOSPHONIUM</b>				<b>NITRO</b>				DMSO:
CH <sub>3</sub> OPh		(49)		P <sup>+</sup> H <sub>4</sub>		-14		RNO <sub>2</sub>				JACS <u>97</u> , 7007 (1975)
MeOCH <sub>2</sub> SO <sub>2</sub> Ph		(30.7)		MeP <sup>+</sup> H <sub>3</sub>		2.7		R= CH <sub>3</sub>	≈10			JACS <u>97</u> , 7160 (1975)
PhOCH <sub>2</sub> SO <sub>2</sub> Ph		(27.9)		Et <sub>3</sub> P <sup>+</sup> H		9.1		CH <sub>2</sub> Me				JACS <u>97</u> , 442 (1975)
PhOCH <sub>2</sub> CN		(28.1)		Ph <sub>3</sub> P <sup>+</sup> CH <sub>3</sub>		(22.4)		CHMe <sub>2</sub>				JACS <u>105</u> , 6188 (1983)
		(21.1)		Ph <sub>3</sub> P <sup>+</sup> i-Pr		(21.2)		CH <sub>2</sub> Ph				JOC <u>41</u> , 1883 (1976)
<b>SELENIDES</b>				<b>PHOSPONATES &amp; PHOSPHINE OXIDES</b>				<b>IMINES</b>				JOC <u>41</u> , 1885 (1976)
PhSe		(18.6)										JOC <u>41</u> , 2786 (1976)
PhSeCHPh <sub>2</sub>		(27.5)		X= Ph		(27.6)		n= 3				JOC <u>41</u> , 2508 (1976)
(PhSe) <sub>2</sub> CH <sub>2</sub>		(31.3)		CN		(16.4)		4				JOC <u>42</u> , 1817 (1977)
PhSeCH <sub>2</sub> Ph		(31.0)		CO <sub>2</sub> Et		(18.6)		5				JOC <u>42</u> , 321 (1977)
PhSeCH=CHCH <sub>2</sub> SePh		(27.2)		Cl		(26.2)		6				JOC <u>42</u> , 326 (1977)
<b>AMMONIUM</b>				SiMe <sub>3</sub>		(28.8)		7				JOC <u>43</u> , 3113 (1978)
Me <sub>3</sub> N <sup>+</sup> CH <sub>2</sub> X								n= 4				JOC <u>43</u> , 3095 (1978)
X= CN		(20.6)		X= SPh		(24.9)		5				JOC <u>43</u> , 1764 (1978)
SO <sub>2</sub> Ph		(19.4)		CN		(16.9)		6				JOC <u>45</u> , 3325 (1980)
COPh		(14.6)		<b>PHOSPHINES</b>				7				JOC <u>45</u> , 3305 (1980)
CO <sub>2</sub> Et		(20.6)		Ph <sub>2</sub> PCH <sub>2</sub> PPh <sub>2</sub>		(29.9)		n= 6				JOC <u>45</u> , 3884 (1980)
CONEt <sub>2</sub>		(24.9)		Ph <sub>2</sub> PCH <sub>2</sub> SO <sub>2</sub> Ph		(20.3)		7				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
<b>Water:</b>												
Advanced Org. Chem., 3rd Ed. J. March (1985)												
Unpublished results of W. P. Jencks												
<b>THF:</b>												
JACS <u>110</u> , 5705 (1988)												

\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.