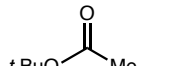
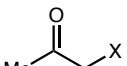
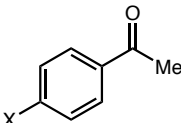
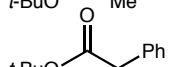
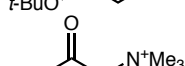
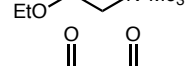

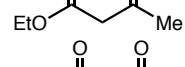
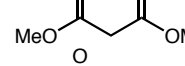
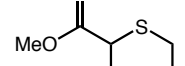
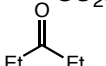

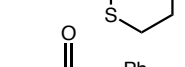
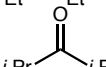
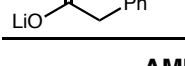
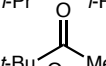
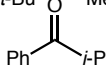
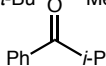
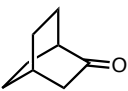
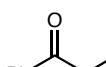
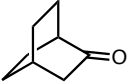
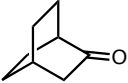
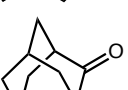
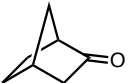
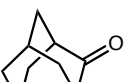
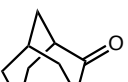


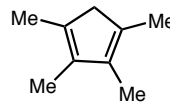
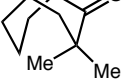
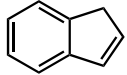



Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O(DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
INORGANIC ACIDS			CARBOXYLIC ACIDS			ALCOHOLS			PROTONATED SPECIES		
H ₂ O	15.7	(32)				HOH	15.7	(31.2)			-12.4
H ₃ O ⁺	-1.7		X= CH ₃	4.76	(12.3)	MeOH	15.5	(27.9)			-7.8
H ₂ S	7.00		CH ₂ NO ₂	1.68		<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
HCl	-8.0	(1.8)	CCl ₃	0.65		<i>m</i> -O ₂ NC ₆ H ₄ OH	8.4				0.79 (+1.63)
HF	3.17	(15)	CF ₃	-0.25		<i>p</i> -O ₂ NC ₆ H ₄ OH	7.1	(10.8)			(+5.55)
HOCl	7.5		H	3.77		<i>p</i> -OMeC ₆ H ₄ OH	10.2	(19.1)			
HClO ₄	-10		HO	3.6, 10.3		2-naphthol		(17.1)			
HCl	-8.0	(1.8)	C ₆ H ₅	4.2	(11.1)	OXIMES & HYDROXAMIC ACIDS					
HF	3.17	(15)	<i>o</i> -O ₂ NC ₆ H ₄	2.17			11.3	(20.1)			
HOCl	7.5		<i>m</i> -O ₂ NC ₆ H ₄	2.45			8.88	(13.7)			
HClO ₄	-10		<i>p</i> -O ₂ NC ₆ H ₄	3.44			(NH)				
HCl	-8.0	(1.8)	<i>o</i> -ClC ₆ H ₄	2.94				(18.5)			
HF	3.17	(15)	<i>m</i> -ClC ₆ H ₄	3.83		PEROXIDES					
HOCl	7.5		<i>p</i> -ClC ₆ H ₄	3.99		MeOOH	11.5				
HClO ₄	-10		<i>o</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄	1.37		CH ₃ CO ₃ H	8.2				
HCl	-8.0	(1.8)	<i>p</i> -(CH ₃) ₃ N ⁺ C ₆ H ₄	3.43							
HF	3.17	(15)	<i>p</i> -OMeC ₆ H ₄	4.47							
HOCl	7.5										
HClO ₄	-10		R= H	4.25							
HCl	-8.0	(1.8)	<i>trans</i> -CO ₂ H	3.02, 4.38							
HF	3.17	(15)	<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.

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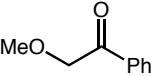
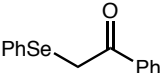
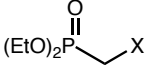
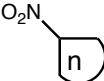
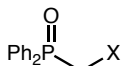
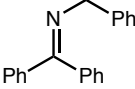
Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)
HYDROCARBONS			ESTERS			KETONES					
(Me) ₃ CH	53			24.5	(30.3)						
(Me) ₂ CH ₂	51				(23.6)	X= H		(26.5)	X= H		(24.7)
CH ₂ =CH ₂	50				(20.0)	Ph		(19.8)	OMe		(25.7)
CH ₄	48	(56)			(20.0)	SPh		(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)			(20.9)			(28.3)	n= 4		(25.1)
Ph ₂ CH ₂	33.5	(32.2)			[30.2 (THF)]			(27.7)	5		(25.8)
Ph ₃ CH	31.5	(30.6)	AMIDES					(26.3)	6		(26.4)
HCCH	24				(26.6)	X= H		(24.7)	7		(27.7)
PhCCH	23	(28.8)			(25.9)	CH ₃		(24.4)	8		(27.4)
XC ₆ H ₄ CH ₃					(24.9)	Ph		(17.7)			(28.1)
X= <i>p</i> -CN		(30.8)			(24.9)	COCH ₃		(14.2)			(29.0)
<i>p</i> -NO ₂		(20.4)			(17.2)	COPh		(13.3)			(25.5)
<i>p</i> -COPh		(26.9)			(18.2)	CN		(10.2)			
		(26.1)			(25.7)	F		(21.6)			(32.4)
	20	(20.1)				OMe		(22.85)			
	15	(18.0)				OPh		(21.1)			
H ₂	~36					SPh		(16.9)			
						SePh		(18.6)			
						NPh ₂		(20.3)			
						N ⁺ Me ₃		(14.6)			
						NO ₂		(7.7)			
						SO ₂ Ph		(11.4)			

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

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Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	Substrate	pKa	H ₂ O (DMSO)	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)					NO ₂	(7.1)	
	(26.7)			(30.5)		R= Me	(27.6)		SMe	(23.5)	
	(25.2)		X= Ph	(30.7)		<i>i</i> -Pr	(30.7)		SPh	(20.5)	
	(30.2)		CO ₂ Me	(20.8)			(24.5)		SO ₂ Ph	(12.2)	
	(30.0)		CN	(19.1)			(33)		PPh ₂	(20.2)	
			RSCH ₂ CN				(14.4)			(22.3)	
			R= Me	(24.3)			(14.4)			(31.1)	
			Et	(24.0)						(18.8)	
			<i>i</i> -Pr	(23.6)			(20.7)			(21.8)	
			<i>t</i> -Bu	(22.9)						(26.6)	
			PhSCH=CHCH ₂ SPh	(26.3)						(32.8)	
			BuSH	10-11	(17.0)					(14.3)	
			PhSH	≈7	(10.3)						

*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 Water: Advanced Org. Chem., 3rd Ed. J. March (1985) Unpublished results of W. P. Jencks THF: JACS <u>110</u> , 5705 (1988) See cited website below for additional data
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		CH ₂ SO ₂ Ph	(7.1)	
(PhSe) ₂ CH ₂	(31.3)			CH ₂ COPh	(7.7)	
PhSeCH ₂ Ph	(31.0)	X= Ph	(27.6)			
PhSeCH=CHCH ₂ SePh	(27.2)	CN	(16.4)	n= 3	(26.9)	
AMMONIUM		CO ₂ Et	(18.6)	4	(17.8)	
Me ₃ N ⁺ CH ₂ X		Cl	(26.2)	5	(16.0)	
X= CN	(20.6)	SiMe ₃	(28.8)	6	(17.9)	
SO ₂ Ph	(19.4)			7	(15.8)	
COPh	(14.6)	X= SPh	(24.9)	IMINES		
CO ₂ Et	(20.0)	CN	(16.9)		(24.3)	
CONEt ₂	(24.9)	PHOSPHINES		Oxime ethers are ~ 10 pka units less acidic than their ketone counterparts Streitwieser, JOC 1991, 56, 1989		
		Ph ₂ PCH ₂ PPh ₂	(29.9)			
		Ph ₂ PCH ₂ SO ₂ Ph	(20.2)			

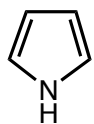
*Values <0 for H₂O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

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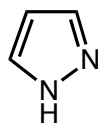
DMSO Acidities of Common Heterocycles

Bordwell, ACR, 1988, 21, 456

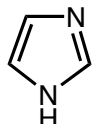
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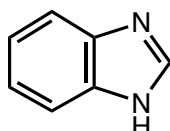
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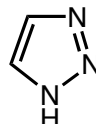
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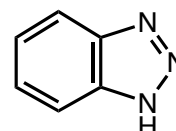
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16.4



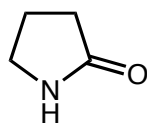
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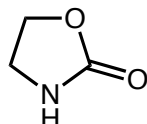
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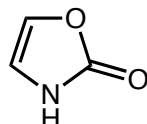
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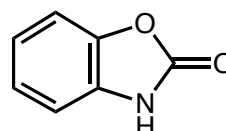
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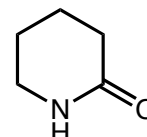
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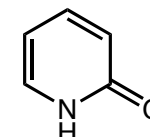
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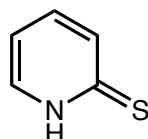
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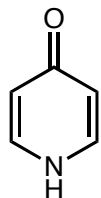
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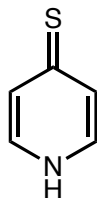
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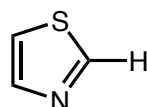
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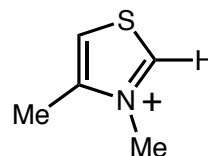
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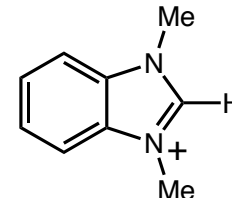
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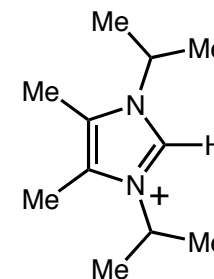
29.4



16.5



18.4



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