

EQUILIBRIUM CONSTANTS FOR HETEROCYCLIC CATION - PSEUDOBASE EQUILIBRATION

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A tabular compilation of pK_{R^+} values is presented for cation-pseudobase equilibration by both heteroaromatic cations and non-aromatic heterocyclic cations in both aqueous and alcoholic solution. Acid dissociation constants (pK_{R^-}) are also given for alkoxide ion formation by heterocyclic pseudobases in aqueous solution.

The phenomenon of pseudobase formation by the covalent addition of hydroxide ion to unsaturated heterocyclic cations in aqueous solution was first recognized by Decker¹ and Hantzsch.^{2,3} This concept has proved useful in the structure elucidation of many heterocyclic cations, and pseudobases are often proposed as intermediates in the mechanisms of a wide variety of reactions of heterocyclic molecules. The general chemistry of heterocyclic pseudobases has been treated in several reviews.⁴⁻⁶

For the equilibrium between the quaternary heterocyclic cation (Q^+) and the corresponding pseudobase (QOH),



an association constant, K , may be defined by equation (2).

$$K = \frac{[QOH]}{[^-OH][Q^+]} \quad (2)$$

This same equilibrium may also be expressed as



with an equilibrium constant, K_{R^+} , which is defined by equation (4) and has the form of a classical Bronsted-acid ionization constant. Combination of equations

$$K_{R^+} = \frac{[H^+][QOH]}{[Q^+]} \quad (4)$$

(2) and (4) gives $K = K_{R^+}/K_w$, where K_w is the ionic product of water. The

heterocyclic cation - pseudobase equilibrium is exactly analogous to the carbonium ion-carbinol equilibrium for which K_{R^+} was originally defined by Deno et al.⁷ The value of pK_{R^+} denotes the pH at which the equilibrium concentrations of the heterocyclic cation and its pseudobase are equal (i.e., $[QOH]/[Q^+] = 1$). Experimental techniques for the spectrophotometric or potentiometric determination of pK_{R^+} values for stable cation-pseudobase equilibria are identical to the methods for the determination of pK_a values for Bronsted acids.⁸

In strongly basic aqueous solutions, the pseudobase species may undergo a deprotonation reaction to form an alkoxide ion (equation (5)).



This equilibrium may be represented by the acid ionization constant, K_- (equation (6)).

$$K_- = \frac{[H^+][QO^-]}{[QOH]} \quad (6)$$

Equilibria analogous to equation (1) can also be established in alcoholic solutions of unsaturated heterocyclic alcohols. In such solvents (ROH), the pseudobases (QOR) are formed by covalent addition of the alkoxide ion (^-OR) to the heterocyclic cation (Q^+). Equilibrium constants, K and K_{R^+} , analogous to equations (2) and (4) may also be defined and measured in alcoholic solutions. In general, cation-pseudobase equilibria tend to favour the pseudobases to a greater extent in alcoholic solution than in aqueous solution. These solvent effects have been considered in some detail in a recent review.⁶ It should also be noted that studies of pseudobase formation in mixed aqueous-alcoholic solvents are complicated by the presence of mixtures of alkoxy and hydroxy pseudobase species from the competition of alkoxide and hydroxide ions for the heterocyclic cations.

During the preparation of a recent review⁶ on heterocyclic pseudobases, an extensive collection of K , pK_{R^+} and pK_- values for a wide variety of heterocyclic cations was compiled from the literature. It was only possible to include a very limited amount of this quantitative data for cation-pseudobase equilibration in that earlier review.⁶ A complete compilation of this equilibrium data is now presented in the following tables, in the hope that it will be a useful set of reference data for all heterocyclic chemists who are engaged in investigations of reactions of heterocyclic cations. No attempt is made to consider structure-equilibrium constant correlations in the present work, since such correlations

have been considered in detail in the earlier review.⁶

Tables 1 and 2 contain pK_{R+} values in aqueous solution for heteroaromatic cations and non-aromatic heterocyclic cations, respectively. Table 3 contains pK_- values for pseudobase anion formation. In Table 4 the limited amount of quantitative data (K and/or pK_{R+}) currently available for pseudobase formation in alcoholic solvents is collected. In all Tables, the data refer to equilibria in the vicinity of 20-25°C unless indicated otherwise. It should be noted that the temperature dependences of pK_{R+} values for cation-pseudobase equilibration in aqueous solution are strongly influenced by the relatively steep temperature dependence of K_w , the ionic product of water.⁹

While I have attempted to produce a comprehensive compilation of data in the following tables, I must apologise in advance to any workers whose contributions to this area may have been overlooked inadvertently.

TABLE 1
 pK_{R^+} VALUES FOR HETEROAROMATIC CATIONS^a

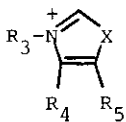
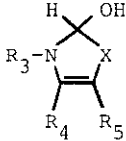
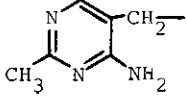
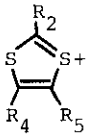
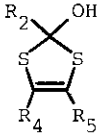
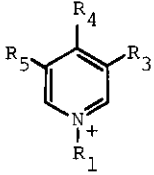
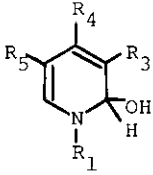
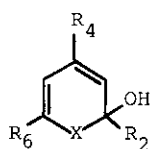
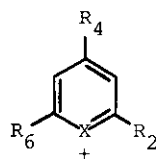
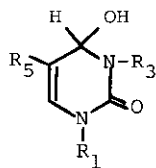
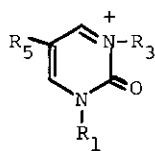
Cation	Pseudobase			pK_{R^+}	Reference
					
R ₃	R ₄	R ₅	X		
	CH ₃	H	O	5.8	10
"	CH ₃	CH ₂ CH ₂ OH	O	5.8	10
CH ₃	H	CH ₃	S	10.8	11
					
R ₂	R ₄	R ₅			
H	C ₆ H ₅	H		2.2 ^b , 2.10 ^c	12, 13
H	4-CH ₃ OC ₆ H ₄	H		2.59 ^c	13
H	4-CH ₃ C ₆ H ₄	H		2.43 ^c	13
H	4-BrC ₆ H ₄	H		1.73 ^c	13
H	4-NO ₂ C ₆ H ₄	H		0.84 ^c	13
H	C ₆ H ₅	C ₆ H ₅		1.8 ^b	12
C ₆ H ₅	C ₆ H ₅	H		4.4 ^b	12
					
R ₁	R ₃	R ₄	R ₅		
CH ₃	COCH ₃	H	H	13.3 ^d	14
4-NO ₂ C ₆ H ₄	NO ₂	H	H	8.0 ^d	15

TABLE 1 (cont'd)

2,6-Cl ₂ C ₆ H ₃	NO ₂	H	H	8.2 ^d	15
CH ₃	CN	H	CN	3.5	16
CH ₃	CN	CN	CN	-1.0	16

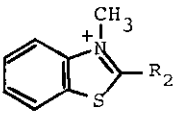
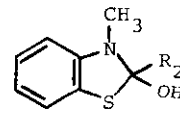
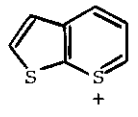
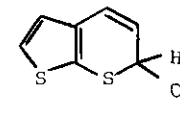
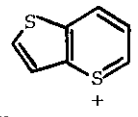
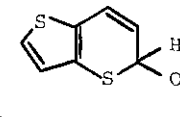
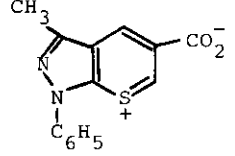
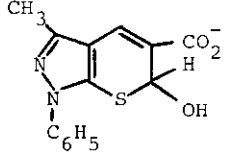


R ₂	R ₄	R ₆	X		
CH ₃	CH ₃	CH ₃	O	6.7 ^{de} , 7.6 ^{def}	17
CH ₃	C ₆ H ₅	C ₆ H ₅	O	6.2 ^{de}	17
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	O	5.0 ^{de}	17
H	H	H	S	>6, 8.7	18, 19



R ₁	R ₃	R ₅		
CH ₃	CH ₃	H	7.03, 7.11, 7.16	20-23
CH ₃	CH ₃	Br	3.08	20
CH ₃	C ₂ H ₅	H	7.21	20
CH ₃	(CH ₃) ₂ CH	H	7.49	20
CH ₃	(CH ₃) ₃ C	H	8.41	20
CH ₃	C ₆ H ₅	H	4.87	20
CH ₃	cyclo-C ₆ H ₁₁	H	7.62	20
CH ₃	C ₆ H ₅ CH ₂	H	6.49	20
C ₂ H ₅	C ₂ H ₅	H	7.49	20
CH ₃ (CH ₂) ₂	CH ₃ (CH ₂) ₂	H	7.42	20
(CH ₃) ₂ CH	(CH ₃) ₂ CH	H	7.94	20
CH ₃ (CH ₂) ₃	CH ₃ (CH ₂) ₃	H	7.58	20

TABLE 1 (cont'd)

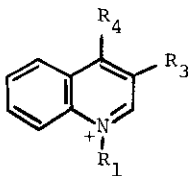
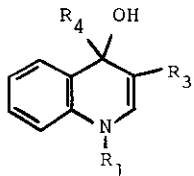
		$R_2 = H$	8.30 ^e	24
		$R_2 = CH_3$	10.30 ^e	24
			6.3	25
			7.0	25
			0.29	26

R_1	R_3	R_5	R_6	R_7	R_8		
CH ₃	H	H	H	H	H	~16.5	27
CH ₃	NO ₂	H	H	H	H	9.16	28
CH ₃	H	NO ₂	H	H	H	12.04, 12.3	29, 30
CH ₃	H	H	NO ₂	H	H	10.80	29
CH ₃	H	H	H	NO ₂	H	11.78	29
CH ₃	H	H	H	H	NO ₂	9.67	29
CH ₃	Br	H	H	H	H	12.1	30
CH ₃	H	Br	H	H	H	13.8	30
CH ₃	H	H	CH ₃ O	H	H	>15	30
CH ₃	H	H	Cl	H	H	>15	30
CH ₃	H	H	Br	H	H	~15	30
CH ₃	H	H	C ₆ H ₅	H	H	>15	30
CH ₃	H	H	H	H	CH ₃ O	>15	30
CH ₃	Br	H	Br	H	H	11.3	30
CH ₃	H	NO ₂	H	NO ₂	H	8.46	31

TABLE 1 (cont'd)

CH ₃	H	H	NO ₂	H	NO ₂	5.61	30
CN	H	H	H	H	H	-0.86, -1.05	30, 32
CN	Br	H	H	H	H	-5.19	30
CN	CH ₃	H	H	H	H	-1.08	30
CN	H	Br	H	H	H	-3.26	30
CN	H	NO	H	H	H	-5.29	30
CN	H	CH ₃ O	H	H	H	-0.33	30
CN	H	H	Cl	H	H	-2.62	30
CN	H	H	Br	H	H	-2.67	30
CN	H	H	NO ₂	H	H	-6.02	30
CN	H	H	CH ₃	H	H	-0.24	30
CN	H	H	CH ₃ O	H	H	+0.41	30
CN	H	H	C ₆ H ₅	H	H	-1.15	30
CN	H	H	H	Br	H	-2.55	30
CN	H	H	H	CH ₃	H	+0.14	30
CN	H	H	H	CH ₃ O	H	+1.37	30
CN	H	H	H	H	CH ₃ O	-1.82	30
C ₂ H ₅	H	H	H	H	NO ₂	9.83	29
NH ₂ COCH ₂	H	H	H	H	H	11.54	29
C ₆ H ₅ CH ₂	H	H	H	H	H	>14	29
C ₆ H ₅ CH ₂	H	NO ₂	H	H	H	11.26	31
3-FC ₆ H ₄ CH ₂	H	NO ₂	H	H	H	11.02	31
4-BrC ₆ H ₄ CH ₂	H	NO ₂	H	H	H	11.05	31
3-CNC ₆ H ₄ CH ₂	H	NO ₂	H	H	H	10.60	31
4-CNC ₆ H ₄ CH ₂	H	NO ₂	H	H	H	10.49	31
4-CH ₃ C ₆ H ₄ CH ₂	H	NO ₂	H	H	H	11.77	31
4-NO ₂ C ₆ H ₄ CH ₂	H	H	H	H	H	11.91	29
4-NO ₂ C ₆ H ₄ CH ₂	H	NO ₂	H	H	H	10.36	31

TABLE 1 (cont'd)

					
R ₁	R ₃	R ₄			
CH ₃	NO ₂	H	6.74, 6.82	27, 28	
CH ₃	H	NO ₂	5.31	33	

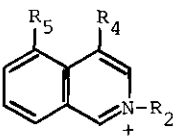
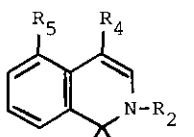
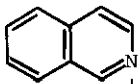
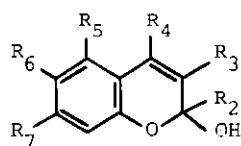
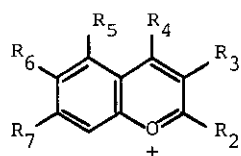
					
R ₂	R ₄	R ₅			
CH ₃	H	H	-15.3, 16.29 ^g	27, 34, 35	
CH ₃	NO ₂	H	5.03, 5.73 ^f	27, 36	
CH ₃	H	NO ₂	11.7	29	
CH ₃	Br	H	-13.5, 13.81	30, 37	
CH ₃	H	Br	-13.7	30	
CN	H	H	-2.0	32	
CN	Br	H	-3.68	30	
CN	H	Br	-3.57	30	
C ₂ H ₅	H	NO ₂	11.8	29	
CNCH ₂	H	H	10.04	29	
CNCH ₂	H	NO ₂	7.26	29	
NH ₂ COCH ₂	H	H	12.1	29	
NH ₂ COCH ₂	H	NO ₂	9.77	29	
CH ₃ (CH ₂) ₂	H	NO ₂	11.84	29	
CH ₃ CH ₂ CH(CH ₃)	H	NO ₂	12.61	29	
2,4-(NO ₂) ₂ C ₆ H ₃	H	H	8.6	30	
C ₆ H ₅ CH ₂	H	H	>14	29	
C ₆ H ₅ CH ₂	H	NO ₂	10.93, 11.29	29, 31	
3-FC ₆ H ₄ CH ₂	H	NO ₂	10.90	31	
4-BrC ₆ H ₄ CH ₂	H	NO ₂	11.05	31	

TABLE 1 (cont'd)

4-CH ₃ C ₆ H ₄ CH ₂	H	NO ₂		11.40	31
3-CNC ₆ H ₄ CH ₂	H	NO ₂		10.60	31
4-CNC ₆ H ₄ CH ₂	H	NO ₂		10.52	31
4-CH ₃ OC ₆ H ₄ CH ₂	H	NO ₂		11.62	31
3-CF ₃ C ₆ H ₄ CH ₂	H	NO ₂		10.79	31
4-NO ₂ C ₆ H ₄ CH ₂	H	H		11.94	29
4-NO ₂ C ₆ H ₄ CH ₂	H	NO ₂		10.40	31
C ₆ H ₅ COCH ₂	H	NO ₂		-8.1	29
	H	H	n = 2	10.84	38
	H	H	n = 3	≥12	38



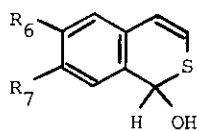
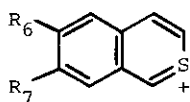
R ₂	R ₃	R ₄	R ₅	R ₆	R ₇		
H	H	H	H	H	H	-1.96	18, 39
H	H	H	H	Cl	H	-3.44	39
H	H	H	H	H	Cl	-3.24	39
H	H	H	H	Br	H	-3.58	39
H	H	H	H	H	Br	-3.31	39
H	H	H	H	CH ₃	H	-1.03	39
H	H	H	H	H	CH ₃	-0.73	39
H	H	H	H	CH ₃ O	H	-0.65	39
H	H	H	H	CH ₃ S	H	-1.97	39
H	H	H	H	H	CH ₃ S	-0.68	39
C ₆ H ₅	H	H	H	H	H	+3.01	40
4-CH ₃ C ₆ H ₄	H	H	H	H	H	+3.65	40
4-CH ₃ OC ₆ H ₄	H	H	H	H	H	+4.47	40
4-HOC ₆ H ₄	OG1 ^h	H	OH	H	OH	2.98	41
4-HO-3,5-(CH ₃ O) ₂ C ₆ H ₂	OG1 ^h	H	OG1 ^h	H	OH	1.85 ⁱ	42

TABLE 1 (cont'd)

R ₂	R ₄					
C ₆ H ₅	H				4.93	40
4-CH ₃ C ₆ H ₄	H				5.54	40
4-CH ₃ OC ₆ H ₄	H				6.64	40
C ₆ H ₅	4-(CH ₃) ₂ NC ₆ H ₄				~7	43
					0.60 ^j	44
R ₂	R ₃	R ₄	R ₆	R ₇		
H	H	H	H	H	3.15	18, 45, 46
H	H	H	Cl	H	1.95	46
H	H	H	H	Cl	1.86	46
H	H	H	Br	H	1.74	46
H	H	H	H	Br	1.66	46
H	H	H	CH ₃	H	4.09	46
H	H	H	H	CH ₃	4.09	46
H	H	H	CH ₃ O	H	4.39	46
H	H	H	H	CH ₃ O	4.95	46
H	H	H	CH ₃ S	H	3.40	46
H	H	H	H	CH ₃ S	4.16	46
C ₆ H ₅	H	H	H	H	5.90	45
H	C ₆ H ₅	H	H	H	2.33	45
H	H	C ₆ H ₅	H	H	3.58	45

TABLE 1 (cont'd)

3-BrC ₆ H ₄	H	H	H	H	4.96	45
H	H	3-BrC ₆ H ₄	H	H	2.93	45
4-BrC ₆ H ₄	H	H	H	H	5.30	45
H	H	4-BrC ₆ H ₄	H	H	3.16	45
H	H	3-CH ₃ C ₆ H ₄	H	H	3.72	45
4-CH ₃ C ₆ H ₄	H	H	H	H	6.39	45
H	H	4-CH ₃ C ₆ H ₄	H	H	3.87	45
3-CH ₃ OC ₆ H ₄	H	H	H	H	5.75	45
H	H	3-CH ₃ OC ₆ H ₄	H	H	3.43	45
4-CH ₃ OC ₆ H ₄	H	H	H	H	6.90	45
H	H	4-CH ₃ OC ₆ H ₄	H	H	4.11	45
3-CH ₃ SC ₆ H ₄	H	H	H	H	5.45	45
H	H	3-CH ₃ SC ₆ H ₄	H	H	3.33	45
4-CH ₃ SC ₆ H ₄	H	H	H	H	6.55	45
H	H	4-CH ₃ SC ₆ H ₄	H	H	3.73	45



R ₆	R ₇		
H	H	2.17	18,47
Cl	H	1.30	47
H	Cl	0.86	47
CH ₃	H	3.54	47
H	CH ₃	3.13	47
CH ₃ O	H	4.88	47
H	CH ₃ O	3.24	47
H	CH ₃ S	2.43	47

TABLE 1 (cont'd)

			1.20	18
			0.20	48
		R ₅ = H	11.04	27
		R ₅ = NO ₂	7.87	37
			8.62 ^k	27
			≤7	27
			~7	49
			12.67	27
			4.93, 5.2	29, 50
			12.33	27

TABLE 1 (cont'd)

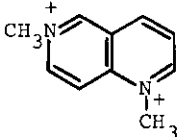
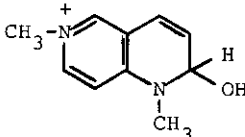
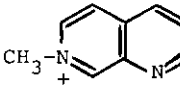
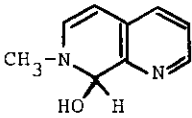
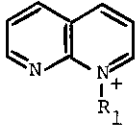
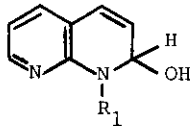
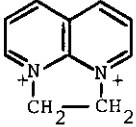
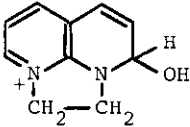
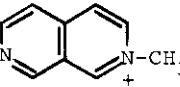
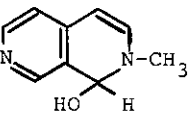
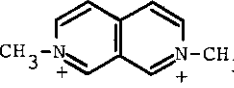
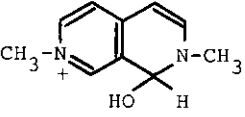
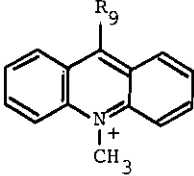
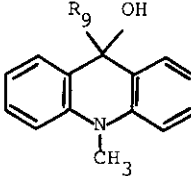
		2.15	29
		13.1	27
		$R_1 = \text{CH}_3$ 12.44	27
		$R_1 = \text{C}_2\text{H}_5$ 12.81	29
		$R_1 = \text{CH}_3(\text{CH}_2)_2$ 12.81	29
		$R_1 = (\text{CH}_3)_2\text{CH}$ 13.7	29
		$R_1 = \text{NH}_2\text{COCH}_2$ 9.83	29
		$R_1 = 4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2$ 10.88	29
		$R_1 = \text{C}_6\text{H}_5\text{COCH}_2$ 7.98	29
		2.2	50
		10.52	29
		3.84	29
		$R_9 = \text{H}$ 9.75, 9.86	27, 51
		$R_9 = \text{C}_2\text{H}_5$ 9.99	52
		$R_9 = \text{C}_6\text{H}_5$ 11.03 ¹	36
		$R_9 = \text{CO}_2^-$ <13	54
		$R_9 = 10\text{-methyl-9-acridinio}$ 12.43	55

TABLE 1 (cont'd)

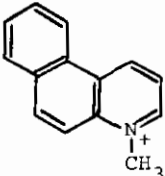
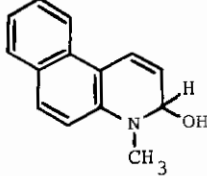
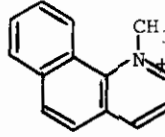
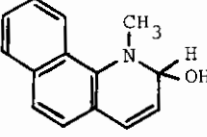
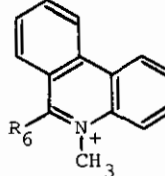
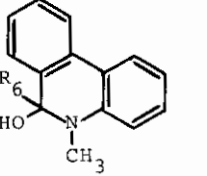
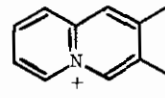
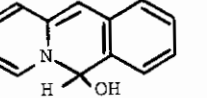
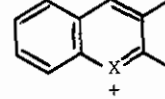
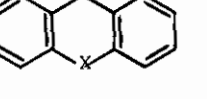
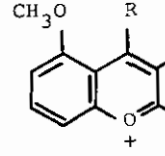
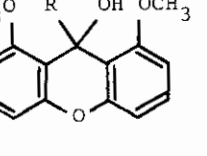
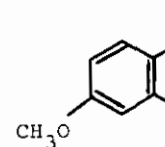
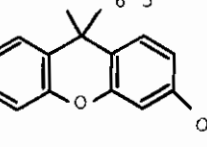
			>14	52
			>14	52
		$R_6 = H$ $R_6 = CH_3$ $R_6 = C_6H_5$	11.94, 10.4 10.1 ~13.5	52, 56 56 52
			~8 ^d	57
		$X = O$ $X = S$ $X = Se$	-0.83 -0.21 -1.67	18 18 18
		$R = 2,6-(CH_3O)_2-$ C_6H_3	2.5	58
			5.44	59

TABLE 1 (cont'd)

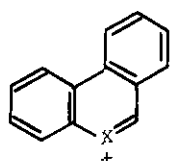
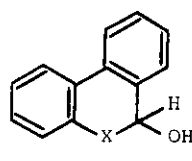
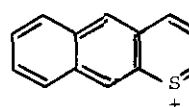
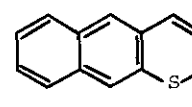
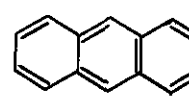
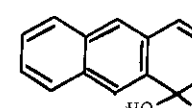
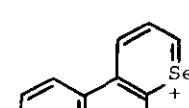
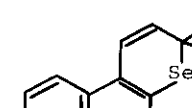
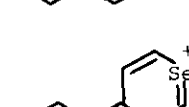
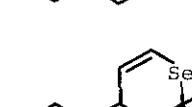
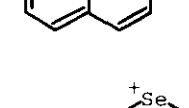
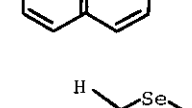
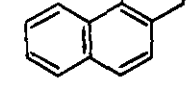
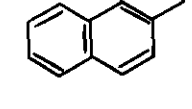
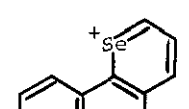
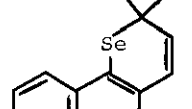


		X = O	-5.96	18
		X = S	-1.67	18
		X = Se	-4.28	18
			1.14	60
			0.33	60
			2.70	61
			1.97	61
			2.39	61
			1.88	61
			9.9 ^d	62
				

TABLE 1 (cont'd)

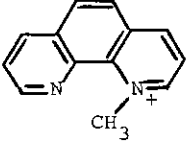
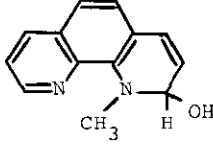
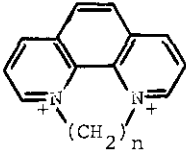
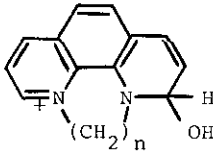
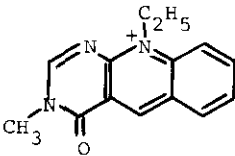
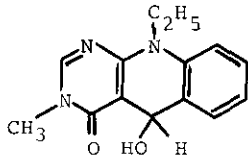
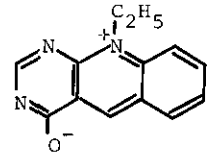
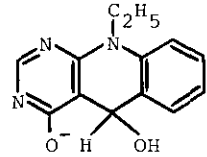
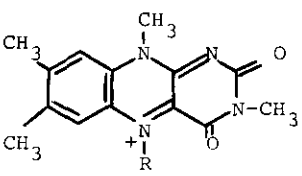
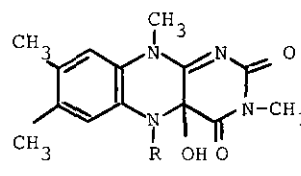
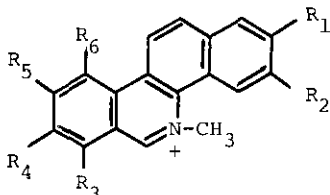
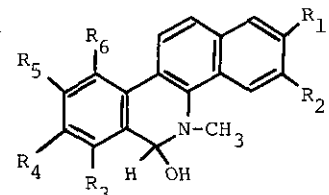
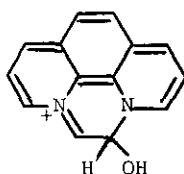
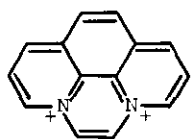
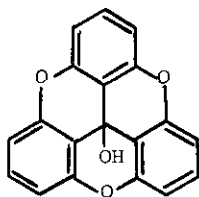
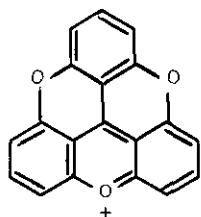
		>14	38				
		n = 2 n = 3	9.54 9.17 38 38				
		8.31	63,64				
		11.3	64				
		R = CH ₃ R = C ₂ H ₅	4.15 4.1 65 66				
<hr/>							
							
R ₁	R ₂	R ₃	R ₄	R ₅	R ₆		
CH ₃ O	CH ₃ O	H	H	H	H	>7	67
H	H	H	CH ₃ O	CH ₃ O	H	>7	67
CH ₃ O	CH ₃ O	H	H	CH ₃ O	H	>7	67
O - CH ₂ - O	O - CH ₂ - O	H	H	H	H	>7, 6.7	67, 68

TABLE 1 (cont'd)

O-CH ₂ -O	CH ₃ O	CH ₃ O	H	H	>7	67	
O-CH ₂ -O	H	CH ₃ O	CH ₃ O	H	>7	67	
HO	CH ₃ O	H	CH ₃ O	CH ₃ O	H	>7	67
CH ₃ O	CH ₃ O	H	CH ₃ O	CH ₃ O	H	>7	67
CH ₃ O	(CH ₃) ₂ CHO	H	CH ₃ O	CH ₃ O	H	>7	67
CH ₃ O	CH ₃ O	CH ₃ O	CH ₃ O	H	CH ₃ O	>7	67
CH ₃ O	CH ₃ O	H	CH ₃ O	CH ₃ O	CH ₃ O	>7	67



6.22, -6.8 38,69



9.05 58

^aIn aqueous solution, at 20-35°C unless otherwise indicated

^bIn 10% dimethylformamide/90% water

^cIn 10% methanol/90% water

^dPseudobase structure not definitely established

^eFrom kinetic measurements

^fIn D₂O

^gIn dimethyl sulfoxide-water

^hGl = 1-α-D-glucopyranosyl

ⁱat 4°C

^jIn 50% ethanol/50% water

^kApparent pK_{R+} - see reference 27

^lK = 1.1 x 10⁻⁶ M⁻¹ in 37.5% acetone/62.4% water⁵³

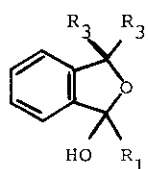
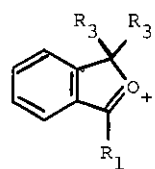
TABLE 2
 pK_{R^+} VALUES FOR NON-AROMATIC HETEROCYCLIC CATIONS^a

Cation		Pseudobase		pK_{R^+}	Reference
R_2	R'_2	R_3	R_5		
CH_3	CH_3	C_6H_5	$(CH_3)_3C$	1.66	70
CH_3	CH_3	C_6H_5	C_6H_5	2.97	70
CH_3	CH_3	C_6H_5	$4-CH_3C_6H_4$	3.73	70
CH_3	CH_3	C_6H_5	$4-CH_3OC_6H_4$	4.47	70
CH_3	CH_3	$4-CH_3C_6H_4$	C_6H_5	3.52	70
CH_3	C_6H_5	C_6H_5	C_6H_5	1.84	70
<hr/>					
				12.2 ^b	71, 72
<hr/>					
R_2		R_4	R_5		
cyclopropyl		H	H	1.1, 1.8	73
C_6H_5		H	H	0.1, -0.5	73, 74
C_6H_5		CH_3	CH_3	1.4	75
$4-FC_6H_4$		H	H	0.2	73
$4-CH_3C_6H_4$		H	H	0.7	73
$4-CH_3OC_6H_4$		H	H	1.1, 1.2, 1.8	73, 74

TABLE 2 (cont'd)

		<-2	76	
		>9.5	77	
R ₁	R ₂	R ₃		
C ₆ H ₅	C ₆ H ₅	CH ₃	10.44, ^c 10.35 ^d	78, 79
C ₆ H ₅	4-CH ₃ OC ₆ H ₄	CH ₃	10.87 ^d	79
C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	7.30	80
3-ClC ₆ H ₄	C ₆ H ₅	CH ₃	9.24 ^d	79
4-ClC ₆ H ₄	C ₆ H ₅	CH ₃	9.60 ^d	79
3-CH ₃ C ₆ H ₄	C ₆ H ₅	CH ₃	10.53 ^d	79
4-CH ₃ C ₆ H ₄	C ₆ H ₅	CH ₃	10.74, ^c 10.83 ^d	78, 79
4-CH ₃ C ₆ H ₄	C ₆ H ₅	C ₆ H ₅	7.66	80
3-CH ₃ OC ₆ H ₄	C ₆ H ₅	CH ₃	10.01 ^d	79
4-CH ₃ OC ₆ H ₄	C ₆ H ₅	CH ₃	11.19, ^c 11.30 ^d	78, 79
4-CH ₃ OC ₆ H ₄	C ₆ H ₅	C ₆ H ₅	8.20	80
4-(CH ₃) ₂ NC ₆ H ₄	C ₆ H ₅	CH ₃	12.03, ^c 12.70 ^d	78, 79
4-(CH ₃) ₂ NC ₆ H ₄	C ₆ H ₅	C ₆ H ₅	9.30	80

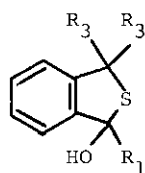
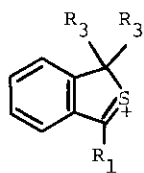
TABLE 2 (cont'd)



R ₁	R ₃		
CH ₃	CH ₃	-2.46	81
C ₆ H ₅	CH ₃	-1.77, -1.71	81-84
C ₆ H ₅	C ₂ H ₅	-0.94	84
C ₆ H ₅	(CH ₃) ₂ CH	+0.71	85
C ₆ H ₅	C ₆ H ₅	-3.74	86
3-FC ₆ H ₄	CH ₃	-2.86	83, 87
3-FC ₆ H ₄	C ₂ H ₅	-2.20	88
4-FC ₆ H ₄	CH ₃	-1.68	83, 87
4-FC ₆ H ₄	C ₂ H ₅	-0.91	88
2-ClC ₆ H ₄	CH ₃	-2.78, -2.91	82, 89
3-ClC ₆ H ₄	CH ₃	-2.96	82, 83, 90
3-ClC ₆ H ₄	C ₂ H ₅	-2.30	88
4-ClC ₆ H ₄	CH ₃	-2.18	82, 83
4-ClC ₆ H ₄	C ₂ H ₅	-1.59	88
2-BrC ₆ H ₄	CH ₃	-2.73	89
3-BrC ₆ H ₄	CH ₃	-2.98	83, 91
3-BrC ₆ H ₄	C ₂ H ₅	-2.41	88
4-BrC ₆ H ₄	CH ₃	-2.37	83, 91
4-BrC ₆ H ₄	C ₂ H ₅	-1.76	88
2-CH ₃ C ₆ H ₄	CH ₃	-0.29, -0.31	84, 89
2-CH ₃ C ₆ H ₄	C ₂ H ₅	+0.72	84
2-CH ₃ C ₆ H ₄	(CH ₃) ₂ CH	+2.06	85
3-CH ₃ C ₆ H ₄	CH ₃	-1.48	83, 84
3-CH ₃ C ₆ H ₄	C ₂ H ₅	-0.79	84
3-CH ₃ C ₆ H ₄	(CH ₃) ₂ CH	+0.96	85
4-CH ₃ C ₆ H ₄	CH ₃	-0.76, -0.83	81, 83, 84
4-CH ₃ C ₆ H ₄	C ₂ H ₅	+0.05	84
4-CH ₃ C ₆ H ₄	(CH ₃) ₂ CH	+1.64	85

TABLE 2 (cont'd)

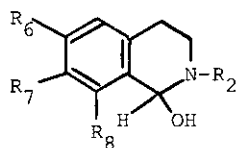
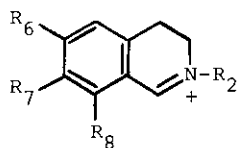
2-CH ₃ OC ₆ H ₄	CH ₃	-0.95, -0.98	89, 92
2-CH ₃ OC ₆ H ₄	C ₂ H ₅	+0.03	88
3-CH ₃ OC ₆ H ₄	CH ₃	-2.12	83
3-CH ₃ OC ₆ H ₄	C ₂ H ₅	-1.45	88
4-CH ₃ OC ₆ H ₄	CH ₃	+0.56, +0.58	81, 83
4-CH ₃ OC ₆ H ₄	C ₂ H ₅	+1.38	88
C ₆ H ₅ CH=CH	CH ₃	+1.08	93
2-C ₂ H ₅ OC ₆ H ₄	CH ₃	-1.04, -1.07	89, 92
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	+0.58	89, 92
4-(CH ₃) ₂ NC ₆ H ₄	CH ₃	+4.94	94
1-naphthyl	CH ₃	-0.71	84, 85
1-naphthyl	C ₂ H ₅	-0.01	84
1-naphthyl	(CH ₃) ₂ CH	+0.72	85
2-naphthyl	CH ₃	-1.46	83, 84, 95
2-naphthyl	C ₂ H ₅	-0.82	84
2-naphthyl	(CH ₃) ₂ CH	+0.58	85
4-(C ₂ H ₅) ₂ NC ₆ H ₄	CH ₃	+5.14	94
4-C ₆ H ₅ C ₆ H ₄	CH ₃	-1.44	83, 84, 95
4-C ₆ H ₅ C ₆ H ₄	C ₂ H ₅	-1.07	84
4-C ₆ H ₅ C ₆ H ₄	(CH ₃) ₂ CH	+0.84	85
9-anthracyl	CH ₃	+1.9	96



R ₁	R ₃		
C ₆ H ₅	CH ₃	-0.72	97
C ₆ H ₅	C ₆ H ₅	-3.15	97
3-FC ₆ H ₄	CH ₃	-1.60	94
4-FC ₆ H ₄	CH ₃	-0.61	94
3-ClC ₆ H ₄	CH ₃	-1.63	94
4-ClC ₆ H ₄	CH ₃	-1.24	98

TABLE 2 (cont'd)

3-BrC ₆ H ₄	CH ₃	-1.81	94
4-BrC ₆ H ₄	CH ₃	-1.34	98
2-CH ₃ C ₆ H ₄	CH ₃	+0.34	94
3-CH ₃ C ₆ H ₄	CH ₃	-0.41	98
4-CH ₃ C ₆ H ₄	CH ₃	+0.22	98
2-CH ₃ OC ₆ H ₄	CH ₃	+0.76	94
3-CH ₃ OC ₆ H ₄	CH ₃	-0.74	94
4-CH ₃ OC ₆ H ₄	CH ₃	+1.22	98
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	+1.23	98
4-(CH ₃) ₂ NC ₆ H ₄	CH ₃	+5.42	94
4-(C ₂ H ₅) ₂ NC ₆ H ₄	CH ₃	+5.60	94



R ₂	R ₆	R ₇	R ₈		
CH ₃	H	H	H	10.75, 10.9	34, 35, 68
3-FC ₆ H ₄ CH ₂	H	H	H	10.21	99
4-BrC ₆ H ₄ CH ₂	H	H	H	10.25	99
3-CNC ₆ H ₄ CH ₂	H	H	H	9.73	99
4-CNC ₆ H ₄ CH ₂	H	H	H	9.74	99
4-NO ₂ C ₆ H ₄ CH ₂	H	H	H	9.55	99
CH ₃	O — CH ₂ — O		CH ₃ O	12.0, 12.4	68, 100
C ₆ H ₅	O — CH ₂ — O		CH ₃ O	8.0	68
4-CH ₃ OC ₆ H ₄	O — CH ₂ — O		CH ₃ O	9.1	68

^aIn aqueous solution at 20-25°C unless otherwise indicated.

^bFrom kinetic measurements.

^cIn 20% acetone/80% water.

^dIn 30% dioxane/70% water.

TABLE 3
pK_a VALUES FOR PSEUDOBASE ANION FORMATION

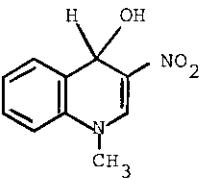
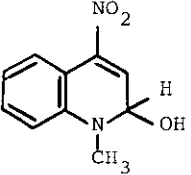
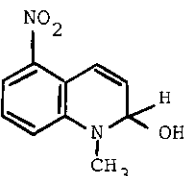
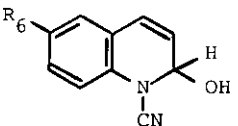
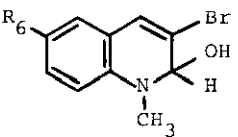
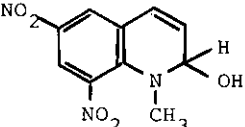
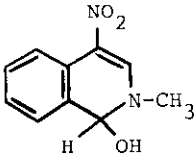
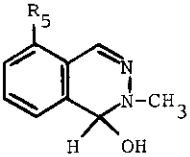
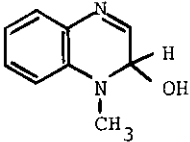
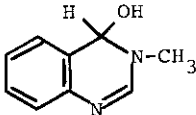
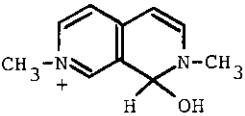
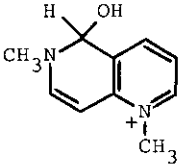
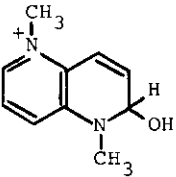
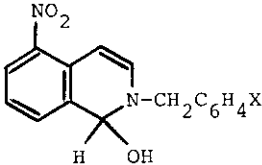
Pseudobase	pK _a	Reference
	13.0	27
	10.95 ^a	33
	~15	30
	R ₆ = H 11.4, 11.2 OCH ₃ 11.8 CH ₃ 11.6 C ₆ H ₅ 11.6 Br 11.6 NO ₂ 9.7	30, 101 30 30 30 30 30
	R ₆ = H ~15 Br ~15	30 30
	14.3	30

TABLE 3 (cont'd)

		11.15	27
	$R_5 = H$	13.0	27
	NO_2	12.10	37
		12.62 ^a	27
		12.47	27
		10.9	29
		11.72	29
		11.75	29
		b	102

^a Apparent pK_a only; anion arises from pseudobase indicated.

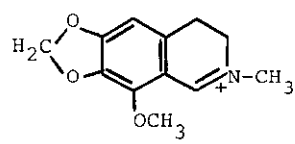
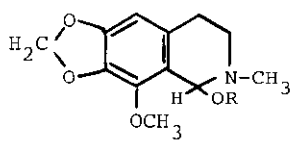
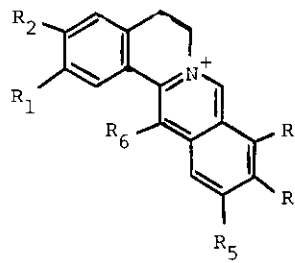
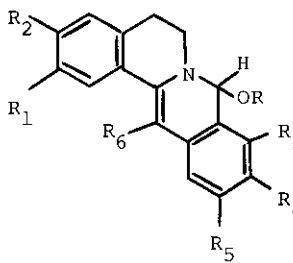
^b See reference 102 for data in 20% acetonitrile/80% water.

TABLE 4

Equilibrium Constants for Pseudobase Formation in Alcoholic Solution^a

Cation	Pseudobase	R	X	K (M ⁻¹)	pK _R ⁺	Reference
		CH ₃			16.9	34
		CH ₃			8.2	34
		CH ₃	4-CH ₃	0.85	17.0	103
				525 ^b		104
		CH ₃	H	1.70	16.7	103
		CH ₃	4-Br	17.0	15.7	103
		CH ₃	3-Cl	40.8	15.3	103
		CH ₃	3-NO ₂	389	14.3	103
		CH ₃	4-NO ₂	2570	13.5	103
		C ₂ H ₅	4-CH ₃	266		103
		C ₂ H ₅	H	700		103
		C ₂ H ₅	4-Br	5095		103
		CH ₃		3.5x10 ⁶		105
		CH ₃	H	>10 ⁷		105
		CH ₃	CH ₃ O	3.2x10 ⁶		105
		CH ₃			7.3	34

TABLE 4 (cont'd)

		C_2H_5	4.7×10^3	100
				
$R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$	CH_3	14.3	106	
$R_1 = R_2 = R_3 = R_4 = OCH_3, R_5 = R_6 = H$	CH_3	15.7	106	
$R_1 + R_2 = OCH_2O, R_3 = R_4 = OCH_3, R_5 = R_6 = H$	CH_3	15.4	106	
	C_2H_5	3.8×10^3	100	
$R_1 + R_2 = R_3 + R_4 = OCH_2O, R_5 = R_6 = H$	CH_3	13.8	106	
$R_1 + R_2 = R_3 + R_4 = OCH_2O, R_5 = H, R_6 = CH_3$	CH_3	15.2	106	
$R_1 = R_2 = OCH_2O, R_3 = R_4 = OCH_3, R_5 = H, R_6 = CH_3$	CH_3	16.5	106	
$R_1 + R_2 = OCH_2O, R_3 = R_4 = R_6 = OCH_3, R_5 = H$	CH_3	16.4	106	

^aData at 20-25°C. See references 12 (1,3-dithiolium cations), 44 and 108 (2-benzopyrylium cations), 67 (benzophenathridinium cations) and 107 (1-phenylpyridinium cations) for data in aqueous-alcoholic media.

^bIn 1:1 methanol-dimethyl sulfoxide.

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