

TABLE 2 — EFFECT OF ADDED ELECTROLYTES ON THE RATES OF SOLVOLYSIS IN AQUEOUS ALCOHOLS

RCl(0.5M)	$10^4 k_1(\text{sec}^{-1})$ (normal)	% of k_1 in the presence of		
		NaCl (0.1M)	NaNO ₃ (0.1M)	LiClO ₄ (0.1M)
70% Aq. ETHANOL (35°C)				
Me ₃ CCl	1.23	+4.9	+9.8	+17.1
Et ₃ CCl	2.83	+2.1	+11.0	+23.3
80% Aq. ETHANOL (45°C)				
Me ₃ CCl	1.07	+6.5	+14.0	+22.4
Et ₃ CCl	2.70	+7.0	+15.9	+31.1
80% Aq. METHANOL (40°C)				
Me ₃ CCl	1.38	+6.5	+11.6	+18.8
Et ₃ CCl	6.34	+7.1	+14.0	+23.2
90% Aq. METHANOL (40°C)				
Me ₃ CCl	0.349	+14.6	+21.2	+28.9
Et ₃ CCl	1.96	+9.7	+17.4	+27.6

are as follows: *t*-butyl: 0.1M NaBr, +82.5, 0.1M LiClO₄, +74.3; Et₃CCl: 0.1M NaBr, +54.2, 0.1M LiClO₄, +65.1%. The salts will exist mainly as ion pairs and this will lead to (a) reduced effect on the initial state, (b) reduced ionic atmosphere effect, and (c) stabilization of the transition state due to dipole-dipole interaction¹⁵.

The rate data in aqueous alcoholic solvents (Table 2) can be interpreted in terms of the ionic atmosphere effect, salt-induced medium effect, and solvent structure-induced ion-pairing effect. The effect of first factor should be larger while that of the other two should be smaller with decrease in water content of the medium.

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Estimation of pK_{BH^+} of Some Mesoionic Thiones

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Apparent second order rate constants (k'_2) for the reactions between mesoionic thiones and chloroacetate are determined in 50% (v/v) buffer-methanol mixture at pH = 3.40, temp. = 30° and $\mu=0.1$. These were in turn used for estimating pK_{BH^+} values with the help of a regression equation $\log k'_2 = 2.3322 + 0.7745(pK_{BH^+})$. Calculated data are in accord with the experimental values.

EARLIER we described¹ a kinetic approach to determine pK_{BH^+} of some mesoionic thiones using the following regression equation,

$$\log k'_2 = 2.3322 + 0.7745(pK_{BH^+}) \quad \dots(1)$$

where $r = 0.989$, std dev. = 0.108 and k'_2 is the apparent second order rate constant for reactions with chloroacetic acid. It was also suggested that this equation might be profitably utilized to predict the pK_{BH^+} of other mesoionic thiones which are not amenable to direct experimental conditions for pK_{BH^+} determinations. As pK_{BH^+} reflects an important intrinsic property of a system and only a limited number of compounds have been examined so far², it was decided to examine the scope and validity of Eq. (1) in the light of additional experimental data with other mesoionic compounds recently reported by us^{3,4}.

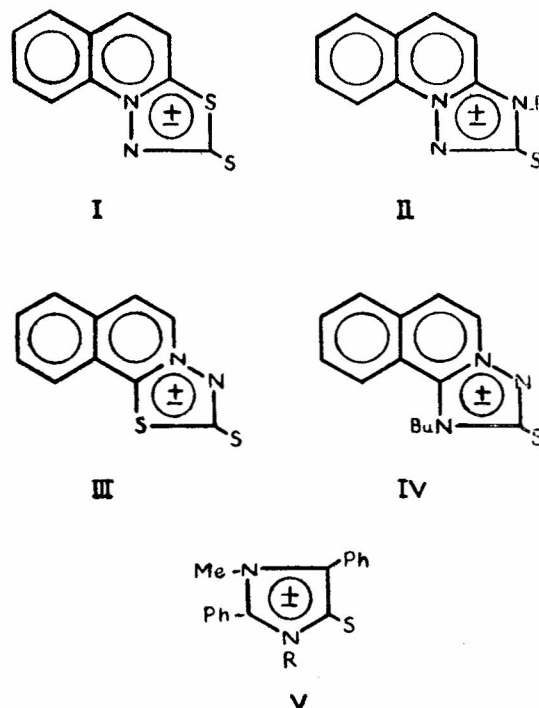


TABLE 1 — pK_{BH^+} OF MESOIONIC THIONES IN 50% *v/v* AQ. METHANOL AT 25°

Compd	λ_{max} (nm)	$10^6 k_{obs}$ sec ⁻¹	$10^6 k'_2$ mole ⁻¹ sec ⁻¹	pK_{BH^+}
I	390	4.336	5.868	-2.02
II (R=Me)	355	7.997	10.820	-1.70
II (R= <i>n</i> -Pr)	355	10.660	14.420	-1.52
II (R= <i>n</i> -Bu)	355	9.594	12.980	(-1.58)†
III	375	4.498	6.087	-2.00
IV	340	15.350	20.770	(-1.92)†
V (R=Me)	300	1322	1789	-1.15
V (R= <i>p</i> -MePh)	310	1322	1789	-1.15
VI†	390	45.06	609.8	0.60

† Values obtained by direct determination as per ref. 1.

The pK_{BH^+} values of mesoionic thiones, viz. 1,3,4-thiadiazolo[3,2-*a*]quinolinium-5-thione³ (I), 1-alkyl-1,3,4-triazolo[3,2-*a*]quinolinium-5-thione³ (II, alkyl = Me, *n*-Pr and *n*-Bu), 1,3,4-thiadiazolo[2,3-*a*]isoquinolinium-5-thione³ (III), 1-*n*-Bu-1,3,4-triazolo[2,3-*a*]isoquinolinium-5-thione³ (IV) and 1-substituted 3-methyl-2,4-diphenylimidazolium-5-thione⁴ (V, R = Me and *p*-Me Ph) presented in Table 1 lead to the following conclusions:

(i) Calculated rate constants (k'_2) cover a significantly wide range as expected² for compounds of diverse structural type, and this difference is also adequately reflected in the estimated pK_{BH^+} values from Eq. 1. This is also in accord with observed slope (= 0.7745), and confirms the usefulness of our findings.

(ii) Tricyclic systems (I, II, III and IV), as anticipated, are weaker bases than the monocyclic imidazoles (V) indicating appreciable intranuclear conjugation in I to IV. Stronger basicity of imidazole derivatives is a well-known fact.

(iii) Compounds I and III are isomeric, but the effect of position of sulphur (*endo*) on their pK_{BH^+} values is only marginal. The insertion of =NR fragment *in lieu* of the *endo*-S generally raises the pK_{BH^+} values, and the difference is conspicuous in the case of II. Similar trend in other mesoionic systems has been recorded earlier by us².

(iv) In support of our estimated pK_{BH^+} values derived from Eq. 1, these were directly determined for II (R=*n*-Pr) and III on account of better stabilities of the tricyclic systems under the experimental condition. Agreement between the two sets (Table 1) is indeed quite satisfactory, and the observed difference falls within the estimated standard deviation (± 0.108) justifying the utility of Eq. 1.

The mesoionic compounds (I-V) used were prepared by the literature method^{3,4}.

The dried samples were stored in the desiccator prior to their use. Imidazoles (V) tend to decompose slowly on storage at room temperature and freshly made samples were used for our work. Other reagents, viz. methanol, KCl, chloroacetic acid, H₂SO₄, NaOH, etc., were of AR grade. All spectrophotometric measurements were made with either Hilger UVspec or recording spectrophotometer in 1 cm quartz cells. *pH* measurements were made on a Philips *pH* meter, model PR9405L.

Kinetic runs — Rate measurements were carried out spectrophotometrically under *pseudo* first order conditions at appropriate wavelength (Table 1) determined previously by separate experiments in aq. methanol (50% *v/v*). In all cases the rate constants (k_{obs}) were obtained from duplicate runs in methanol-buffer (chloroacetate) mixtures (at *pH* = 3.40, temp. = 30° and μ = 0.1M) where the [chloroacetic acid] varied from 10² to 10³ moles litre⁻¹ over the [substrate]. Values of k'_2 were derived by dividing k_{obs} with the total molar concentration of the buffer in the reaction medium. Other experimental details and calculations were the same as before¹.

Determination of pK_{BH^+} — Experimental details for pK_{BH^+} determination have been reported earlier². pK_{BH^+} (25°C) values obtained for the two stable systems in 50% *v/v* aq. methanol determined at 355 nm (II, R = *n*-Pr, isosbestic point, 325 ± 2 nm) and at 375 nm (III, isosbestic point 340 ± 2 nm) are also recorded in Table 1.

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Succinimide Complexes of Cu(II), Ni(II), Co(II), Fe(II) & Hg(II)

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Stability constants of succinimide complexes of Fe(II), Co(II), Ni(II), Cu(II) and Hg(II) have been determined and are found to be 3.10, 6.28, 3.30, 6.44 and 6.88 respectively. The solid complexes are non-electrolytes in nitrobenzene and show IR bands due to coordinated hydroxo groups.

METAL-LIGAND stability constants of Cu(II), Ni(II), Co(II), Fe(II) and Hg(II) complexes with succinimide have been determined in aqueous medium using Bjerrum's *pH* titration technique.

Succinimide (BDH) was recrystallized from ethanol. CuCl₂·2H₂O; NiSO₄·6H₂O; Co(NO₃)₂·6H₂O; FeSO₄·7H₂O and HgCl₂ were of AR grade. Carbonate-free KOH was prepared by the method of Davies and Nancollas¹. All the solutions were prepared in doubly distilled water. Physical measurements were carried out as described earlier².

The solid 1:1 and 1:2 metal complexes were prepared by mixing the reactants containing a little excess of succinimide over the calculated amount and adjusting the *pH* to 8.5, 5.8, 7.0, 9.0 and 8.5 in the case of Ni(II), Hg(II), Fe(II), Cu(II) and Co(II) complexes respectively by the addition of KOH. The resulting solutions were heated to ≈ 40° and ethanol added until the precipitates were formed. The precipitates were filtered, washed with 50%