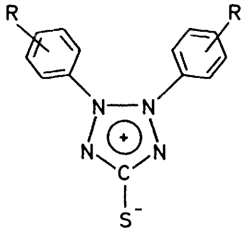
Studies on Mesoionic Compounds. Part 4.† Protonation Equilibria of 2,3-Diaryl-2*H*-tetrazolium-5-thiolates and 1,3,4-Thiadiazolium-2-thiolates in Aqueous Perchloric Acid Solutions

By **A. Mageed Kiwan** * and **Galila A. Wanas**, Department of Chemistry, University of Kuwait, State of Kuwait

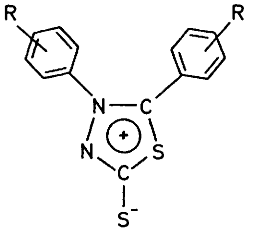
The pK_{BH^+} values of five 2,3-diaryl-2*H*-tetrazolium-5-thiolate and six 1,3,4-thiadiazolium-2-thiolate mesoionic compounds were determined spectrophotometrically in aqueous perchloric acid solutions at 15, 25, 35, and 45 °C. Our results have shown that both types of mesoionic compounds behave as Hammett bases and that protonation was suggested to occur at the exocyclic sulphur atom. The thermodynamic functions ($\Delta G°$, $\Delta H°$, and $\Delta S°$) of ionization have been determined and are discussed.

ALTHOUGH 2,3-diaryl-2*H*-tetrazolium-5-thiolates (I) and 1,3,4-thiadiazolium-2-thiolate (II) mesoionic compounds are formally neutral, their most accepted resonance hybrid structures[1] suggest that they are potentially weak bases. Structure (Ib) has been proved for 2,3-diphenyl-2*H*-tetrazolium-5-thiolate by *X*-ray crystal diffraction, whereas structure (II) has been supported by *X*-ray photoelectron spectroscopy.[2] The charge densities on the nitrogen and sulphur atoms are in satisfying accord with the charge distribution expected for mesoionic structures.



(I)

a; R = 3—CH$_3$
b; R = H
c; R = 4—F
d; R = 3—Cl
e; R = 2—Cl



(II)

a; R = 2—CH$_3$O
b; R = 4—CH$_3$
c; R = H
d; R = 4—F
e; R = 3—Cl
f; R = 4—Cl

Ollis and Ramsden[1] have recently published an authoritative review on the chemistry of these mesoionic compounds, yet little information seems to be available on their protonation. One of us[3] has recently reported some preliminary data on the protonation of a number of derivatives in aqueous hydrochloric acid solution containing 10% v/v ethanol. This paper describes our results of an investigation of the protonation equilibria of five 2,3-diaryl-2*H*-tetrazolium-5-thiolates and six 1,3,4-thiadiazolium-2-thiolates in aqueous perchloric acid solutions at four different temperatures.

EXPERIMENTAL

Materials.—The 2,3-diaryl-2*H*-tetrazolium-5-thiolates (Ia—e) were prepared by oxidizing the freshly prepared 1,5-diarylthiocarbazone ArNH·NH·CS·N : NAr with potassium hexacyanoiron(III) in slightly alkaline medium; details are reported elsewhere.[4] 1,3,4-Thiadiazolium-2-thiolates (IIa—f) were prepared as described elsewhere.[5]

Determination of the Dissociation Constants.—Stock solutions (*ca.* 1 × 10^{-3}M) of each mesoionic compound were prepared by dissolving a weighed sample in absolute ethanol. Portions (0.5 ml) were pipetted into 50 ml volumetric flasks and then diluted to the mark with aqueous perchloric acid solutions of the appropriate concentration. The spectra of these solutions were measured with a Unicam SP 8000 recording spectrophotometer using silica cells and a thermostatically controlled cell block. Measurements were made over the temperature range 15—45 °C and the temperature was controlled to ± 0.05 °C. Ionization ratios (*I*) were obtained from the standard relationship (1) where ε_B, ε_{BH^+},

$$\log I = \log [BH^+]/[B] = \log_{10} [(\varepsilon_B - \varepsilon_{obs})/(\varepsilon_{obs} - \varepsilon_{BH^+})] \quad (1)$$

and ε_{obs} are the molar absorptivities of the unprotonated, fully protonated mesoionic compound, and a mixture of the two, respectively, at a given wavelength close to $\lambda_{max.}$. The reversibility of protonation was checked in each case by dilution of a specimen solution of the protonated mesoionic compound when the spectra of the unprotonated species were obtained. Furthermore, there was never any evidence for decomposition reactions during the time of measurement. Values of $\varepsilon_{B(max.)}$ and $\varepsilon_{BH^+(max.)}$ were obtained from smooth sigmoid curves of total absorbance at $\lambda_{B(max.)}$ and $\lambda_{BH^+(max.)}$ *versus* acid concentration (or H_0). Each value was taken from the beginning of the linear portions at the extremities of each sigmoid curve. Rochester's[6] H_0 values for aqueous perchloric acid solutions were used.

RESULTS AND DISCUSSION

Absorption Spectra.—The electronic spectra of the unprotonated mesoionic compounds (I) and (II) in aqueous solutions show two well defined absorption bands in the region 240—400 nm. The shorter wavelength band (*ca.* 250 nm) was assigned to a $\pi \longrightarrow \pi^*$ transition, whereas the longer wavelength band (*ca.* 390 nm) was assigned to an $n \longrightarrow \pi^*$ transition.[4,5] On increasing the acidity of the aqueous solution, both absorption bands change and were finally replaced by a single band near 300 nm in concentrated perchloric acid solution. The Figure shows a typical example of such a spectral behaviour for (IIa) as the acidity of the aqueous solution changes and Table 1 summarizes the spectral characteristics of the

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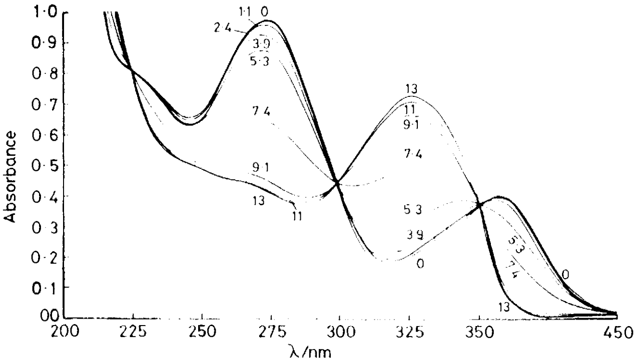
† Part 3, ref. 3.



Absorption spectra of (IIa) (5.12×10^{-5}M) in water (curve 0) at various [$HClO_4^-$] at 25 °C. Molalities are given on the curves

five tetrazolium (Ia—e) and six thiadiazolium (IIa—f) mesoionic compounds.

Ionization Data.—The ionization ratios for (Ia) at 15, 25, 35, and 45 °C are reported in Table 2 as a typical example. Plots of $\log_{10}I$ against H_0 gave straight lines with slopes which were sufficiently close to unity (0.97—1.05) to conclude that the protonation of both 2,3-diaryl-2*H*-tetrazolium-5-thiolate and 1,3,4-thiadiazolium-2-thiolate mesosionic compounds follows the H_0 acidity function at the four temperatures.

TABLE 1

Spectral characteristics of 2,3-diaryl-2*H*-tetrazolium-5-thiolates (Ia—e) and 1,3,4-thiadiazolium-2-thiolates (IIa—f) in aqueous perchloric acid solutions containing 1% v/v ethyl alcohol

Compound	λ_B (max)/nm (ϵ_{max})	λ_{BH^+} (max)/nm (ϵ_{max})	Isosbestic points (nm)
(Ia)	246 (11 840)		282, 355
	370 (880)	324 (2 830)	
(Ib)	247 (25 430)		283, 353
	(1 620)	318 (6 490)	
(Ic)	248 (24 420)		287, 355
	370 (1 880)	325 (6390)	
	250 (21 430)		
	374 (1 290)	322 (3 570)	282, 352
(Ie)	247 (25 310)		
	375 (1 720)	316 (5 310)	282, 352
(IIa)	274 (19 110)		351, 298
	357 (7 800)	326 (14 210)	
(IIb)	273 (15 200)		360, 317
	358 (10 800)	348 (17 200)	
(IIc)	270 (19 750)		344, 294
	365 (6 330)	316 (11 010)	
(IId)	272 (19 360)		344, 293
	364 (6 370)	317 (12 990)	
(IIe)	270 (20 650)		343, 293
	258 (6 090)	312 (10 210)	
IIf)	275 (21 500)		352, 296
	360 (7 250)	310 (14 130)	

TABLE 2

Values of $\log_{10}(C_{BH^+}/C_B)$ as functions of perchloric acid concentration for (Ia) at four temperatures

	C_{BH^+}/C_B			
m_{HClO_4}/mol K^{-1}	15 °C	25 °C	35 °C	45 °C
2.4	−0.94	−0.87	−0.76	−0.62
3.9	−0.33	−0.23	−0.14	−0.07
4.5	−0.11	0.02	0.09	0.16
5.0	0.26	0.36	0.42	0.48
6.5	0.58	0.72	0.78	0.82
7.4	0.84	1.01	1.08	1.17

The pK_{BH^+} values were calculated by equations (2)[7,8]

$$pK_{BH^+} = m(H_0)_{\frac{1}{2}} \qquad (2)$$

[where *m* is the slope of log *I versus* H_0 and $(H_0)_{\frac{1}{2}}$ is H_0 at 50% protonation] and (3). The pK_{BH^+} values

$$\log I + H_0 = \phi(H_0 + \log[H^+]) + pK_{BH^+} \qquad (3)$$

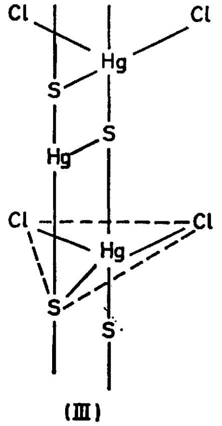
(Table 3) obtained from both equations were closely similar within the experimental error (± 0.06). The ϕ values were found to be close to zero (—0.005 to —0.15) which supports our conclusion that both mesoionic series (I) and (II) behave as Hammett bases.

TABLE 3

Values of $-pK_{BH^+}$ for the conjugate acids of 2,3-diaryl-2*H*-tetrazolium-5-thiolates (Ia—e) and 1,3,4-thiadiazolium-2-thiolates (IIa—f) in aqueous perchloric acid solutions at four temperatures

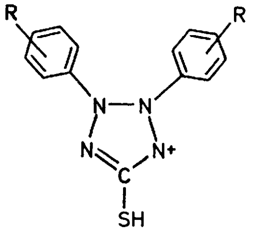
	$-pK_{BH^+}$			
	15 °C	25 °C	35 °C	45 °C
(Ia)	1.83 ± 0.04	1.76 ± 0.02	1.64 ± 0.02	1.55 ± 0.02
(Ib)	1.86 ± 0.02	1.73 ± 0.01	1.62 ± 0.02	1.50 ± 0.01
(Ic)	1.87 ± 0.05	1.80 ± 0.05	1.66 ± 0.01	1.58 ± 0.02
(Id)	1.95 ± 0.02	1.84 ± 0.02	1.71 ± 0.02	1.64 ± 0.02
(Ie)	2.24 ± 0.03	2.10 ± 0.03	2.04 ± 0.02	1.95 ± 0.02
(IIa)	2.08 ± 0.06	2.02 ± 0.02	1.88 ± 0.03	1.80 ± 0.05
(IIb)	2.61 ± 0.04	2.51 ± 0.03	2.42 ± 0.04	2.38 ± 0.04
(IIc)	2.49 ± 0.04	2.41 ± 0.04	2.30 ± 0.05	2.21 ± 0.06
(IId)	2.87 ± 0.03	2.66 ± 0.06	2.60 ± 0.08	2.40 ± 0.10
(IIe)	3.02 ± 0.03	2.91 ± 0.06	2.84 ± 0.06	2.73 ± 0.07
(IIf)	3.11 ± 0.33	3.02 ± 0.08	2.93 ± 0.06	2.80 ± 0.03

Site of Protonation.—Although there is no direct proof of where protonation takes place on these mesoionic compounds, it is expected that the exocyclic sulphur atoms in both (I) and (II) are the most likely sites of protonation as supported by the following evidence. (1) Methylation of both (I)[9] and (II)[10] leads to the formation of exocyclic *S*-methyl derivatives. (2) Species (Ib) reacts with mercury(II) chloride to give a complex (III), the *X*-ray diffraction structure of which was found[11] to have the mercury atom being bonded to the exocyclic sulphur atom in a trigonal-bipyramidal arrangement. (3) The oxygen analogues of (II) were recently



(III)

suggested by Tillet *et al.*[12] to protonate at the exocyclic oxygen atom. Thus, it is reasonable to assume that structures (IV) and (V) are the predominant protonated species of 2,3-diaryl-2*H*-tetrazolium-5-thiolates. Other resonance stabilized structures such as (VI) and (VII), however, may be also formed in aqueous solution.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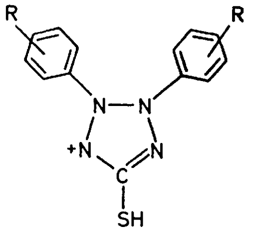
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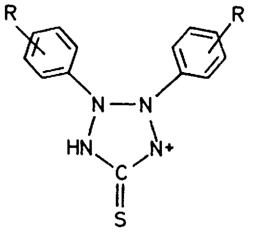
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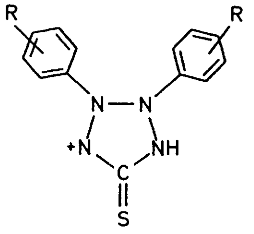
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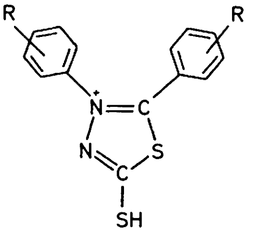
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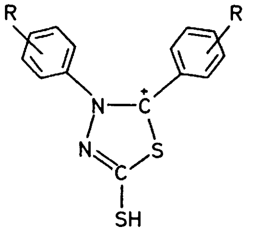
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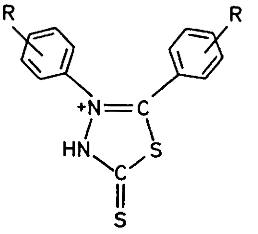
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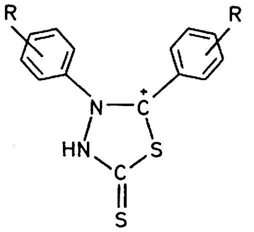
(XI)

The protonated species (VIII) and (IX) may be similarly proposed for the conjugate acids of the mesoionic compounds (II). Minor contributions from (X) and (XI) cannot be excluded in aqueous acidic solutions. However, protonated species which involve cleavage of either the tetrazolium or thiadiazolium five-membered rings must be excluded on thermodynamic grounds.

The effect of substituents on the phenyl groups attached to the tetrazolium or thiadiazolium rings of (I) and (II) could not be assessed accurately here owing to the limited data available. Nevertheless, our results of pK_{BH^+} determinations summarized in Table 3 indicate that the electron-donating methoxy-group in (IIa) has enhanced its basicity, whereas the introduction of the electron-withdrawing chlorine atom in (Id), (Ie), (IIe), and (IIf) has decreased their basisities compared with the unsubstituted mesoioniccompounds.

Thermodynamics of Protonation.—The thermodynamic functions of protonation of the mesoionic compounds were obtained by equation (4).[13] Plots of pK_{BH^+}

$$\log K_{BH^+} = -(\Delta H^\circ/2.303RT) + (\Delta S^\circ/2.303R) = -\Delta G^\circ/2.303RT \quad (4)$$

against $1/T$ were linear indicating that ΔH° was invariant with temperature within the limits of the experimental error.

The slopes and intercepts were deduced by computer using the standard method of least squares. The thermodynamic quantities obtained are summarised in Table 4.

TABLE 4

Thermodynamic functions for the protonation of 2,3-diaryl-2*H*-tetrazolium-5-thiolates (Ia—e) and 1,3,4-thiadiazolium-2-thiolates (IIa—f)

Compound	$-\Delta G^\circ$ (25 °C)/ kJ mol^{-1}	$-\Delta H^\circ$/ kJ mol^{-1}	$-\Delta S^\circ$/ J K^{-1} mol^{-1}
(Ia)	9.94 ± 0.11	15.8 ± 1.5	19.5 ± 5
(Ib)	9.89 ± 0.06	20.9 ± 0.4	36.9 ± 2
(Ic)	10.02 ± 0.29	22.6 ± 2.7	42.1 ± 9
(Id)	10.44 ± 0.11	18.8 ± 3	28.2 ± 4
(Ie)	12.13 ± 0.17	16.4 ± 1.7	14.2 ± 6
(IIa)	11.26 ± 0.11	16.4 ± 1.6	17.1 ± 5
(IIb)	13.8 ± 0.16	14.2 ± 2.1	1.2 ± 0.8
(IIc)	13.7 ± 0.23	14.4 ± 0.8	2.3 ± 1.2
(IId)	15.4 ± 0.34	27.3 ± 4	40.0 ± 13
(IIe)	16.7 ± 0.34	16.5 ± 12	0.6 ± 0.4
(IIf)	17.2 ± 0.46	17.8 ± 1	2.2 ± 1.0

According to Hepler[13] each thermodynamic quantity is associated with internal and environmental effects. The former effects were defined[14] as those intrinsic to the solute, whereas the latter come from solute–solvent interactions. It has also been argued by Bolton and Hepler[15] that for most symmetrical reactions with ΔS° *ca.* 0, the free energy changes are approximately equal to the enthalpy changes which arise from the internal effects (ΔH_{int}). Inspection of the data in Table 4 indicates the following points.

(1) The ΔS° values for 2,3-diaryl-2*H*-tetrazolium-5-thiolates (Ia—e) are considerably negative which indicates the difference in solvation of the unprotonated and protonated molecules in spite of the remarkable polar nature of the former molecules. Differences in the values of ΔG° and ΔH° may also suggest that variations in the free energies of ionization come from both enthalpy and entropy of ionization. The presence of the highly electronegative fluorine atom in (Ic) seems to increase the entropy changes of ionization by increasing the solute–solvent interactions.

(2) The ΔS° values for (IIb, c, e, and f) are close to zero, thus suggesting a close similarity in the solvation of the unprotonated and protonated molecules. The corresponding ΔG° values are almost equal to the ΔH° values

which indicates that the major contribution to the free energies of ionization of these compounds comes from $\Delta H^{\circ}_{\text{int}}$, *i.e.* from the effect of substituents. The presence of the highly electronegative atoms of fluorine and oxygen in (IId and a), respectively, increases the ΔS° considerably (-40 and -17 J K^{-1} mol) through their pronounced influence on the solvation of these compounds. Accordingly, the variations in their ΔG° values come from both ΔH° and ΔS°.

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