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Oxidation of Thiols. IV.[1] The Effect of Substituents on Ionization and Hexacyanoferrate (III) Oxidation of Monothiodiacylmethane

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Ionization constants, pK_a, for a set of six monothiodiacylmethanes have been determined in 50 vol% ethanol–water mixture at 25° ±0.1. Excellent linear correlations are obtained when pK_a values are plotted against the substituent constant, σ_x, and the polar substituent constant, $\sigma^*_{xC_6H_4}$, for substituted phenyl groups. The regression lines are: pK_a=8.00−1.47 σ_x and pK_a=8.92−1.195 $\sigma^*_{xC_6H_4}$, respectively. The pK_a values are also correlated with the extended Hammett equation. The correlation follows the equation:

$$pK_a = 7.717 - 1.330\sigma_{I,x} - 1.248\sigma_{R,x}$$

The rate of the oxidation of (Ie) with hexacyanoferrate(III) was discussed at different pH values.

Keywords——monothiodiacylmethanes; ionization constants; oxidation; ultraviolet spectra; linear free energy relationship

Introduction

Monothiodiacylmethanes (I) have been shown to react as enethiol form (IA).[3-5] However, some workers reported that they exist as enol-thione form (IB) [4,6-11] whereas others have noted their existence as a mixture of enol-enethiol tautomers[4,12-14] (*cf.* Chart 1). Oxidation of this type of compounds gave the corresponding disulphides.[3,4,15]

The Present investigation was intended to study the correlation of ionization constants of (Ia—f) with the simple and extended Hammett equations (1) and (2), respectively,

$$pK_a = -\rho\sigma_x + h \qquad 1)$$

$$pK_a = \propto\sigma_{I,x} + \beta\sigma_{R,x} + h \qquad 2)$$

as well as the rate of the oxidation-reduction reaction with $Fe(CN)_6{}^{3-}$ at different pH, in order to give further insight about the structure of these series of compounds.

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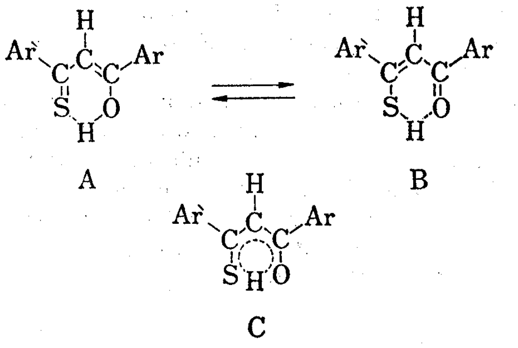

I

	Ar	Ar'
a)	C_6H_5	C_6H_5
b)	p-$CH_3C_6H_4$	C_6H_5
c)	m-ClC_6H_4	C_6H_5
d)	p-ClC_6H_4	C_6H_5
e)	p-$CH_3OC_6H_4$	C_6H_5
f)	C_6H_5	p-ClC_6H_4

Chart 1

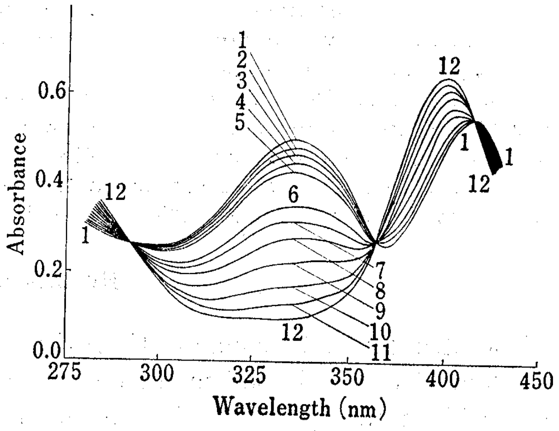

Fig. 1. Absorption Spectra of (Id) at Different pH Values

(3.135×10^{-5} M; in 50 vol% ethanol-water, 25°).

Experimental

Monothiodiacylmethanes (Ia—f)[16] were prepared from the corresponding aroylphenylacetylene according to the method outlined by Badder *et al.*[4] β-Hydroxy-α-thiobenzoylstyrene (Ia), mp 84—85°;[4] yield, 97%; β-hydroxy-α-thiobenzoyl-p-methylstyrene (Ib), mp 130—131°;[4] yield, 98%; β-hydroxy-α-thiobenzoyl-m-chlorostyrene (Ic), mp 98—99°;[4] yield, 91%; β-hydroxy-α-thiobenzoyl-p-chlorostyrene (Id), mp 122—123°;[4] yield, 98%, β-hydroxy-α-thiobenzoyl-p-methoxystyrene (Ie), mp 133—134°;[4] yield, 95%, α-(p-chlorothiobenzoyl)-β-hydroxystyrene (If), mp 118—119°; yield, 88%. *Anal.* Calcd. for $C_{15}H_{11}ClOS$: C, 65.58; H, 4.05; S, 11.67; Cl, 12.90. Found: C, 65.71; H, 4.08; S, 11.83; Cl, 13.09.

Potassium hexacyanoferrate(III) was recrystallised from water and dried. Its stock solution was prepared by weight and standardised spectrophotometrically ($\varepsilon=1030$ mol^{-1} cm^{-1} at 420 nm). Phosphate-sodium hydroxide (carbonate free) buffers were prepared from analytical grade chemicals. In all spectroscopic runs, freshly distilled ethanol was used.

Electronic spectra were taken on a Pye-Unicam SP 8000 Spectrophotometers. The instrument was calibrated as previously described.[17] In the kinetic runs, a SP 700 Spectrophotometer, equipped with thermostated cell holders, was used.

A radiometer pH-meter model 63 fitted with a combined glass electrode type GK 2301C was used for determination of pH. The instrument was accurate to ±0.01 pH unit. It was calibrated using two standard Radiometer buffer solutions at pH 4.01 and 7.00. The pH meter readings (B) recorded in 50% ethanol–water solution were converted to hydrogen ion concentration [H$^+$] by means of the widely known relation of Van Uitert and Haas,[18]

$$-\log[\mathrm{H}^+] = B \pm \log U_\mathrm{H} \qquad 3)$$

where U_H is the correction factor for the solvent composition and ionic strength for which B is read. For this purpose, readings were made on a series of solutions containing known amounts of hydrochloric acid and sodium chloride such that the ionic strength is equal to 0.10 in 50% ethanol–water medium. The intercept, obtained from the linear plot of pH *vs.* B, corresponding to log U_H was found equal to 0.30 ± 0.01 at 25°.

For spectrophotometric determination of the dissociation constants of compounds (Ia—f), an aliquot of the stock solution made by dissolving a known weight of monothiodiacylmethane(I) in ethanol to give an 1.0×10^{-2} M solution, was diluted with aqueous hydrochloric acid and ethanol. The final solution contains accurately about 3.0×10^{-5} M of the compound (I), and 0.10 M HCl in 50% ethanol-water.

The absorption spectra of the solution at constant temperature, (25°) were taken at different pH's by adding carbonate free sodium hydroxide and/or hydrochloric acid in small amounts. Since the total change

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[16] Monothiodiacylmethanes are named as β-hydroxy-α-thiobenzoylstyrene derivatives (IA) because the nuclear magnetic resonance (NMR) spectra of these compounds in $CDCl_3$ or CCl_4 solution show the presence of enol-thione form (IA) only.[4,5—10]

[17] M.S. El-Ezaby and N. Gayed, *J. Inorg. Nucl. Chem.*, **37**, 1065 (1975).

[18] L.G. Van Uitert and C.G. Haas, *J. Am. Chem. Soc.*, **75**, 451 (1953).

in volume did not exceed 1.0%, no correction was made for the concentration of the compounds. The ionic strength was kept constant at 0.10 M HCl/NaCl. Each compound was subjected to three pK_a determinations, and the average values given in Table I are within ±0.01—0.03 pK_a units.

The kinetic runs were performed under pseudo-first order conditions using potassium hexacyanoferrate (III) in large excess (more than tenfold). The ethanolic solution of (Ie) was added to one compartment, and in the other, $Fe(CN)_6^{3-}$, buffer and KCl solutions (to adjust ionic strength) were added. The flask was kept at 25° for 20 minutes and the reactants were thoroughly mixed. An aliquot of the reaction mixture was quickly transferred to a 1 cm quartz cell which was kept in the thermostated cell holder of the spectrophotometer. The change in the absorbance as a function of time was followed at 440 nm, where the magnitude of change was found to be reasonable. The pH of each solution was then measured.

Results and Discussion

The structure and configuration of the compounds (Ia—e) were established previously by Baddar *et al.*[4] and confirmed that the enethiol tautomer is the more reactive part, in the enol/enethiol tautomeric equilibria of monothiodiacylmethanes (*cf.* Chart 1). The ionization constants (pK_a's) of the compounds (Ia—f) and the oxidation of (Ie) with hexacyanoferrate (III) were studied to give another support for the presence of the enethiol tautomer.

(i) Acid Dissociation Constants

The ionization constants (pK_a's) of Ia—f were determined in 50 vol% ethanol–water media (25°±0.1) using the spectrophotometric method at different pH values. The dependence of absorbance on pH is shown in Figure 1 for the compound (Id) at 334 nm. The value of pK_a was calculated for each reading using the following equation,[19]

$$pK_a = pH_x + \log(A_x - A_a)/(A_u - A_x) \qquad 4)$$

where A_x is the absorbance at pH_x, A_a is the absorbance of the anion and A_u is that of the unionized form. The results are summarized in Table I.

Table I. Ionization Constants, pK_a, of Substituted Monothiodiarylmethanes (Ia—f) at 25°, $\mu = 0.10$ M HCl/NaCl in 50 vol% Ethanol–Water and Substituent Constants used in Their Correlation

Compound	pK_a[a)]	σ_x[b)]	$\sigma^*_{xC_6H_4}$	$\sigma_{I,x}$	$\sigma_{R,x}$
Ia	7.71	0.00	0.58	0.00	0.00
Ib	7.93	−0.17	0.46	−0.04	−0.13
Ic	7.21	0.37	0.85	0.46	−0.09
Id	7.45	0.23	0.75	0.46	−0.23
Ie	8.03	−0.27	0.36	0.27	−0.54
If	7.25				

a) Standard deviation+0.02—0.03.
b) C.G. Swain and E.G. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968).

The pK_a values of compounds (Ia—e) were correlated with the simple Hammett equation (1) by two ways. In the first case, the pK_a values were plotted *vs.* the Hammett substituent constant σ_x of the x-substituent, Figure 2A. In the second case, we included the phenyl group with the substituent, and plotted the pK_a values against the polar substituent constant, $\sigma^*_{xC_6H_4}$ for substituent phenyl groups,[20] Figure 2B. Excellent linear relations were obtained in both cases and may be represented by the equations (4) and (5), respectively.

$$pK_a = 8.00 - 1.47\sigma_x \qquad 4)$$

$$pK_a = 8.92 - 1.195\sigma^*_{x\,C_6H_4} \qquad 5)$$

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[19] R.F. Cookson, *Chem. Rev.*, 74, 5 (1974).

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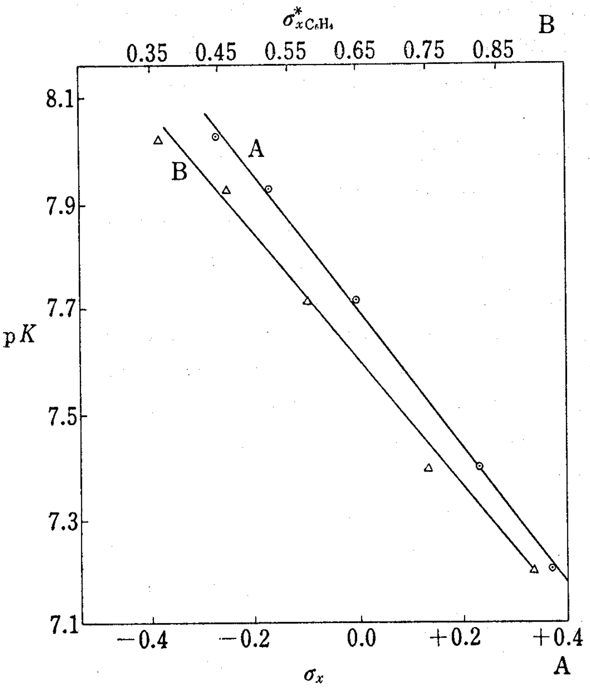

Fig. 2. Correlations of Acid Dissociation Constants (pK_a) of Monothiodiacylmethanes (Ia—e) with the Substituent Constants, σ_x (A) and $\sigma^*_{xC_6H_4}$ (B)

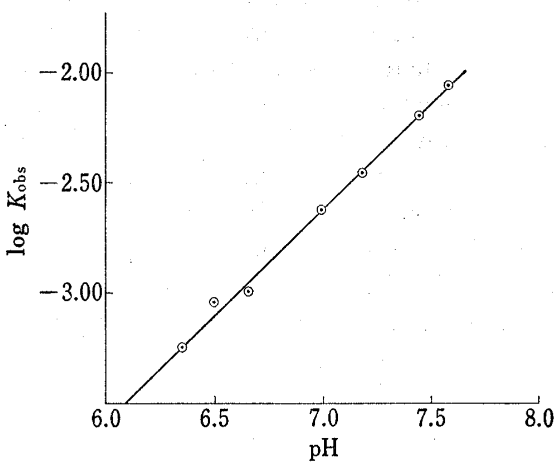

Fig. 3. Correlation of log K_{obs} with pH
[SRH]$=2.34\times10^{-5}$ M, I$=0.0875$ M and [Fe(CN)$_6^{3-}$]$=1\times10^{-3}$ M.

Table II. Results of Correlation with Equation (2)

Parameter	Value	Parameter	Value
α	−1.330	S_α[b]	0.018
β	−1.248	S_β[b]	0.021
h	7.717	S_h[b]	0.006
R[a]	0.999	N[c]	5

a) Multiple correlation coefficient.
b) Standard errors of the estimates: α, β, and h, respectively.
c) Number of points.

Table III. Electronic Absorption Spectra of Monothiodiarylmethanes (Ia—f) in 50 vol% Ethanol-Water Mixture

Compound	Ultraviolet maxima	
	Neutral form λnm ($\varepsilon\times10^3$)	Anion λnm ($\varepsilon\times10^3$)
Ia	411(18.01), 331(15.73), 264 (9.85)	395(21.62), 251(15.13)
Ib	417(19.17), 322(14.65), 272 (7.72)	395(19.97), 269(13.05)
Ic	407(14.96), 336(14.48), 262 (7.90)	400(19.30), 250(12.39)
Id	414(17.54), 334(15.95), 270(11.16)	400(20.57), 263(15.63)
Ie	433(23.05), 334(16.47), 279 (5.49)	394(22.00), 278(11.53)
If	413(17.6), 336(16.00), 266(11.10)	406(20.7), 255(15.5)

The ionization constants were also correlated with the extended Hammett equation (2) by multiple regression analysis.[21] The data used in the correlation are given in Table I and the results are shown in Table II. The value, 0.999, obtained for multiple correlation

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[21] M.R. Spiegel, "Theory and Problems of Statistics," Schaum Publishing Co., N.Y., 1961., p. 269.

coefficient indicates an excellent correlation. The values of α and β, thus obtained indicate that the composition of the electrical effect, E, defined as the ratio β/α has the value 0.938.

These results indicate that the values of pK_a's depend on the type of the substituent present. The higher pK_a value for (Id) compared with that of If may be explained on the fact that the enethiols are the more acidic tautomers. In If the chlorine atom is closer to the sulphur atom and, hence, its effect on the enethiol form ionization is more pronounced.

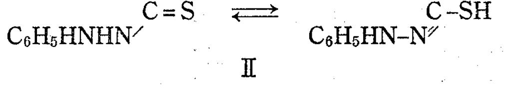
The electronic spectra of the compounds (Ia—f) in 50% ethanol–water mixture are identical and show absorption maxima in the ranges 433—407 nm, 336—322 nm and 279—262 nm (Table III). None of these bands can be attributed to $n \rightarrow \pi^*$ transition since all of them are intense and blue shifted in less polar solvents, *e.g.* cyclohexane.[4] These bands may be assigned to the transitions π–π^* (S=$\dot{C}$–$\dot{C}$=$\dot{C}$–O),[13,14,22] π–π^* (ArCS)[23] + π–π^* (O=$\dot{C}$–$\dot{C}$=$\dot{C}$–S),[13,14] and π–π^* (ArCO),[14,22] respectively. The 330 nm bands are assigned to transition from both the enols and the enethiols.[14] The position of the first two bands is red shifted in comparison with the compounds in which the aryl groups are replaced by *tert*-butyl groups,[22] perhaps due to a high decrease in the conjugation. The electron donating groups in the phenyl rings also, enhance a red shift. On ionization, both bands are blue shifted, perhaps due to the decrease in the conjugation. The longer wavelength band (433—407 nm) may be due to an extended conjugation through the formation of a chelated ring structure, probably arising from an electron-delocalized "quasi-aromatic" (IC), (Chart 1), may be predominant in solution.[14] Such chelate decomposes readily on ionization.

(ii) Kinetics

Monothiodiacylmethane (Ie) was taken as an example in the kinetic study (represented hereafter as RSH). The derivative (Ie) was oxidised to the corresponding disulphide according to the stoichiometric equation (6)

$$2RSH + 2Fe(CN)_6^{3-} \longrightarrow RSSR + 2Fe(CN)_6^{4-} + 2H^+ \qquad 6)$$

The identification of the product and the stoichiometry of the reaction have already been reported.[24] Plots of $\log_{10}(A_t - A_\infty)$ *vs.* time, where A_t and A_∞ correspond to absorbances at time (t) and infinity respectively, obey first order kinetics to beyond 90% of the reaction. The magnitude of the pseudo-first order rate constant, k_{obs} sec^{-1}, is obtained from the slopes $\times 2.303$ and is independent of the concentration of Ie as previously reported by Kassim *et al.*[24] The variation of log K_{obs} with pH, while the other factors remaining constant, is shown in Figure 3. At pH >8, the rate is found to be too fast to be measured by the spectrophotometer. The data represented in Figure 3 show that the reaction is negligibly slow in acid medium and, indeed, when the reaction was carried out at pH<6, the rate found to be negligible. Since the rate of the oxidation-reduction reaction of the unionized form of dithizone (II) (thione form) (Chart 2), which is known to exist[25] in the thione/thiol equilibria, can be studied spectroscopically in acidic medium (pH range 1—2), the failure of compound (Ie) to react at such media may indicate the presence of the enethiol form in our system.



$$\begin{matrix} C_6H_5\text{–}N\text{=}N \\ C_6H_5HNHN \end{matrix} \Big> C\text{=}S \rightleftharpoons \begin{matrix} C_6H_5\text{–}N\text{=}N \\ C_6H_5HN\text{–}N \end{matrix} \Big> C\text{–}SH$$

II

Chart 2

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22) S.H. Chaston and S.E. Livingstone, *Aust. J. Chem.*, **20**, 1079 (1967).
23) G. Oster, L. Citarel, and M. Goodman, *J. Am. Chem. Soc.*, **84**, 703 (1962).
24) A.Y. Kassim, F.H. Al-Hajjar, and Y. Sulfab, *Inorganica Chim, Acta*, **28**, 41 (1978).
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