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Proton Donor Acceptor Interactions of Disubstituted Thiovioluric Acids with Amines Bases

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The stability constants of hydrogen bonded ion pair or proton transfer complex formation of N,N'-dimethyl thiovioluric acid [DMTVA], N,N'-di-*o*-tolyl thiovioluric acid [DOTTVA], N,N'-di-*m*-tolyl thiovioluric acid [DMTTVA] and N,N'-di-*p*-tolyl thiovioluric acid [DPTTVA] with methyl amine, dimethyl amine, trimethyl amine, ethyl amine, diethyl amine, triethyl amine, *n*-butyl amine, dibutyl amine and tributyl amine have been determined spectroscopically in 95 % (v/v) ethanol. The composition of the complexes is determined in solution potentiometrically and spectrophotometrically and substantiated by the element analysis and IR spectra of the isolated complexes. The stabilities of the thiovioluric acid-amine complexes have been correlated with the base strength of amines. The correlation between the mode of enolization in the acids and the structure of the proton transfer complex is discussed. The variation in proton transfer constants of acids has been explained on the basis of the changes in the distribution of electron density in the ring.

Key Words: Proton, Acceptor, Thiovioluric acids, Amines.

INTRODUCTION

The studies on the behaviour of the heterocyclic imines and enols are of current interest in biopolymers and in the physical chemistry of drug action. It is desirable that more information is gathered about similar model systems. Thiovioluric acids containing enolic and imine groups in a benzenoid heterocyclic ring system have been selected as one such model compounds. Violuric acids which form interesting coloured salts with alkaline hydroxides and organic bases have been extensively studied by several workers[1-7] but the thiovioluric acids have been paid little attention. The present work deals with detailed spectrophotometric investigations on the interaction of N,N'-disubstituted thiovioluric acids with a number of aliphatic amines in ethanol-water mixture.

EXPERIMENTAL

N,N'-Disubstituted thiovioluric acids were synthesised by method of Lal and Dutt[8] by the action of nitrous acid on corresponding N,N'-disubstituted thiobarbituric acids. All the acids were used after further purification.

UV and visible spectra were taken with a specord recording spectrophotomerter [Carl-Zeiss] and spectronic-20 [Bausch and Lomb] with 1 cm cells in 95 % ethanol-water mixture as solvent. IR spectra were taken in KBr pellets with a Beckmann IR-20 infrared spectrophotometer. The pH-titrations were performed at 25 ± 0.5 °C using a pH meter [Elico, India] with a precision of 0.20 pH unit.

The complexes of N-N'-di substituted thiovioluric acids with some amines have been isolated in the solid state by the following procedure.

The concentrated solution of N,N'-disubstituted thiovioluric acids prepared in aqueous ethanol was treated with a large excess of respective amine. After about 2 h, the solution was concentrated under reduced pressure at room temperature. Dioxane was added to the solution in order to precipitate the complex. The complex was filtered off, washed with small portions of dioxane-water and dried *in vacuo*. It was assumed that in the presence of large excess of amines, only a trace of unreacted N,N'-disubstituted thiovioluric acid was left in the complex and that the unreacted amine was removed by washing with dioxane-water and prolonged drying *in vacuo*.

RESULTS AND DISCUSSION

The UV-visible spectra of N,N'-dimethyl thiovioluric acid (DMTVA), N,N'-di-*o*-tolyl thiovioluric acid (DOTTVA), N,N'-di-*m*-tolyl thiovioluric acid (DMTTVA) and N,N'-di-*p*-tolyl thiovioluric acid (DPTTVA) in solution strongly depend on the pH of the medium indicating successive deprotonation equilibria. The significant bands of DMTVA are at 265 nm in strongly acidic solution and at 225, 342 and 582-586 nm in alkaline medium. The spectral behaviour of DOTTVA, DMTTVA and DPTTVA with pH is identical with that of DMTVA, but all the UV and visible bonds undergo red shifts by 2-l0 nm.

The solutions of the complexes of DMTVA, DOTTVA, DMTTVA and DPTTVA absorb between 605 and 620 nm and Beer's law is found to be valid at 605 nm for DMTVA, 610 nm for DOTTVA, 620 nm for DPTTVA and 615 nm for DMTTVA. All these thiovioluric acids and amines do not absorb in 95 % ethanol-water mixture. At these wave lengths, the optical density will be proportional to the concentration of the complex. The composition of the complexes and their stability have been determined by limiting logarithmic method[9]. For the reaction.

$$m[\text{amine}] + n[\text{TVA}] \rightleftharpoons [\text{amine}]_m[\text{TVA}]_n$$

The stability constant of complexes of N,N'-substituated thiovioluric acids [TVA] with different amines can be given by

$$K = \frac{[\text{amine}]_m[\text{TVA}]_n}{[\text{amine}]^m[\text{TVA}]^n} \quad (1)$$

Taking logarithms,

$$\log\,[\text{amine}]_m[\text{TVA}]_n = m \log\,[\text{amine}] + n \log\,[\text{TVA}] + \log K \quad (2)$$

The values of m, n and K may be computed graphically from two sets of measurements, one with constant [amine] and variable [TVA] and the other with constant [TVA] and variable [amine]. The stability constants of the complexes and their physical properties are given in Table-1. The last column records the K values corrected for amine ethanol interactions[10].

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF N,N'-DISUBSTITUTED THIOVIOLURIC ACID-AMINE COMPLEXES AT 30 ºC

SI. No.	Complex with	Colours	m.p. ºC	25 ºC pK_b Ref-13	Stability constant [K × 10^{-4}]	-?G Kcal Mol^{-1}	K_s Ref-2	K_{corr} × 10^{-4}
(a) DMTVA-amine complexes, λ_{max} = 615 nm								
1	Methyl amine	Light green	153-155(Dec)	3.36	1.86	5.89	2.42	0.54
2	Dimethyl amine	Brilliant green	133-135(Dec)	3.28	2.23	6.01	3.66	0.47
3	Trimethyl amine	Olive green	168-170(Dec)	3.26	2.45	6.06	3.10	0.59
4	Ethyl amine	Light green	115-117(Dec)	3.25	3.16	6.21	2.60	0.87
5	Diethylamine	Deep green	125-128(Dec)	3.02	3.63	6.30	2.62	1.01
6	Triethylamine	Greenish gray	145-147(Dec)	3.24	4.26	6.39	2.52^a	1.21
7	*n*-Butyl amine	Light green	163-165(Dec)	3.39	2.29	6.02	3.30^a	0.53
8	Dibutyl amine	Olive green	110-112(Dec)	3.44	2.57	6.09	4.37	0.47
9	Tributyl amine	Brilliant green	137-139(Dec)	3.55	2.95	6.17	3.34	0.67
(b) DOTTVA-amine complexes, λ_{max} = 610 nm								
1	Methyl amine	Light green	185-187(Dec)	3.36	2.13	5.98	2.42	0.62
2	Dimethyl amine	Deep green	144-146(Dec)	3.28	2.45	6.06	3.66	0.52
3	Trimethyl amine	Greenish grey	175-177(Dec)	3.26	2.88	6.16	3.10	0.70
4	Ethylamine	Brilliant green	146-148(Dec)	3.25	3.16	6.21	2.60	0.87
5	Diethyl amine	Deep green	113-115(Dec)	3.02	3.71	6.31	2.62	1.02
6	Triethylamine	Olive green	155-157(Dec)	3.24	4.36	6.41	2.52^a	1.23
7	*n*-Butyl amine	Brilliant green	159-162(Dec)	3.39	2.51	6.08	3.30^a	0.58
8	Dibutyl amine	Dark green	137-139(Dec)	3.44	3.02	6.19	4.37	0.56
9	Tributyl amine	Deep olive green	168-170(Dec)	3.55	3.38	6.25	3.34	0.77
(c) DMTTVA-amine complexes, λ_{max} = 605 nm								
1	Methylamine	Light green	195-197(Dec)	3.36	1.86	5.89	2.42	0.54
2	Dimethyl amine	Olive green	135-136(Dec)	3.28	2.23	6.01	3.66	0.47
3	Trimethyl amine	Brilliant green	190-192(Dec)	3.26	2.45	6.06	3.10	0.59
4	Ethyl amine	Greenesh grey	180-182(Dec)	3.25	3.16	6.21	2.60	0.87
5	Diethylamine	Bluish green	165-167(Dec)	3.02	3.63	6.30	2.62	1.01
6	Triethylamine	Light green	185-187(Dec)	3.24	4.26	6.39	2.52^a	1.21
7	*n*-Butyl amine	Deep green	177-179(Dec)	3.39	2.29	6.02	3.30^a	0.53
8	Dibutyl amine	Olive green	144-146(Dec)	3.44	2.57	6.09	4.37	0.47
9	Tributyl amine	Brilliant green	157-160(Dec)	3.55	2.95	6.17	3.34	0.67
(d) DPTTVA-amine complexes, λ_{max} = 620 nm								
1	Methyl amine	Deep olive green	147-149(Dec)	3.36	2.69	6.12	3.42	0.78
2	Dimethyl amine	Brilliant green	132-134(Dec)	3.28	3.09	6.20	3.66	0.66
3	Trimethyl amine	Light green	180-182(Dec)	3.26	3.71	6.31	3.10	0.90
4	Ethylamine	Olive green	115-117(Dec)	3.25	5.01	6.49	2.60	1.39
5	Diethyl amine	Deep green	150-152(Dec)	3.02	5.88	6.59	2.62	1.62
6	Triethylamine	Bluish green	138-140(Dec)	3.24	7.24	6.71	2.52^a	2.05
7	*n*-Butyl amine	Brilliant green	122-124(Dec)	3.39	3.98	6.35	3.30^a	0.92
8	Dibutyl amine	Olive green	144-146(Dec)	3.44	4.78	6.46	4.37	0.89
9	Tributyl amine	Light green	162-164(Dec)	3.55	5.49	6.54	3.34	1.26

K_s = ethanol-amine stability constant, a = estimated value $K_{corr.}$ = K/1 + K_s, Dec = Decomposition.

The 1:1 composition of complexes in solution, inferred from the values of m = 1, n = 1 was further confirmed spectrophotometrically and from pH-metric titrations of N,N'-disubstituted thiovioluric acids with amines and by the elemental analysis of the isolated complexes. The differential plot of ΔpH/ΔV against ΔV invariably showed an inflexion at 1:1 molar ratio. The calculated and observed values for percentage of C, H, N tallied within ± 2.5 %.

The skeletal structures of DMTVA, DOTTVA, DPTTVA and DMTTVA are identical, but they contain different substitutents which cause a great change in the distribution of electron density in the ring and hence the electron density at any particular point is also affected. Consequently the protonation-deprotonation equilibria and the proton-transfer equilibria of these acids in the presence of amines also vary.

In case of N,N'-disubstituted thiovioluric acids, the first dissociation is due to the enolization of carbonyl groups at positions 4 or 6 through the hydrogen atom of oxime group[11]. This enolization is favoured by high electron density at oxygen of the >C=O group, which in turn is enhanced by a partial π-interaction between the neighbouring N atom and C atom of the >C=O group. Such a π-interaction is quite possible, since systems are known[12] in which the lone pair of electron on N atom conjugate the p_z-electrons of the neighbouring carbon atoms. In the case of DMTVA, the N atom is further attached to an electron donating methyl group resulting in an acid weakening effect compared to thiovioluric acid. In the case of DOTTVA, DMTTVA and DPTTVA, since N and N_3 atoms are attached to the phenyl groups, it is likely that the π-interaction also occurs with the aromatic systems. In these acids, however, the extent of this π-interaction with aromatic nucleous would be controlled by the σ donor property of the methyl group. In the case of DPTTVA and DOTTVA, the π-interaction with phenyl nucleous would be inhibited as electron density is enhanced at C_7 due to the electron releasing property of methyl group.

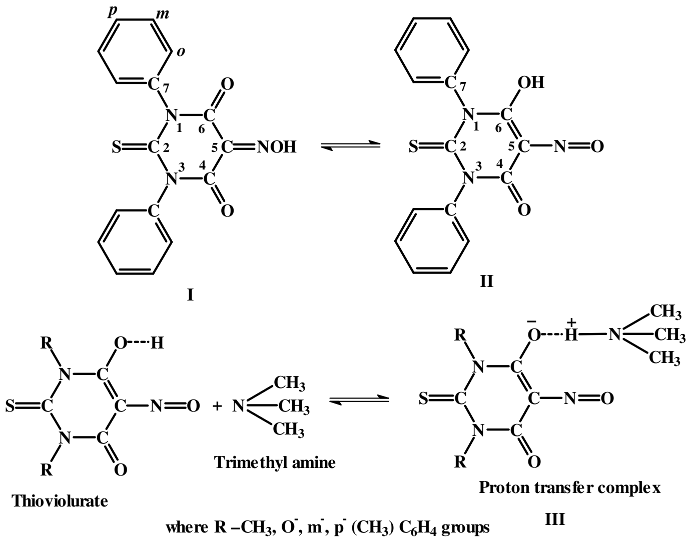
Thus, in the case of DPTTVA, N_1-C_6 π-interaction is greater, leading to greater enolization and hence stabilization of nitro-enolic form, hence, its pKa is higher. The N,-C_6 π-interaction is less for DOTTVA than that for DPTTVA. This is because the methyl group at *ortho* position sterically hinders this π-interaction, giving rise to lesser enolization and possible destabilisation of nitroso-enolic form DMTTVA lies midway between DPTTVA and DOTTVA. Since methyl group is *ortho* and *para* orienting, it can not increase electron density at C_7 and thus does not inhibit the N_1-C_6 π-interaction. This explains its lower pKa as compared to that of DPTTVA. However, the methyl group at *meta* position is further away from N_1 and can not sterically affect π-interaction in any way. This explains its higher pKa value as compared to that of DOTTVA.

Since the ease of removal of a proton is the determinant in both the deprotonation and proton transfer complex formation, the pK_a of the acids and log K of proton-transfer complexes should be related linearly. The N,N'-disubstituted thiovioluric acids, except DOTTVA, do indeed show such a linear relationship between pKa and log K for all the amine systems.

The pK_a order is: DMTVA (4.65) < DOTTVA (4.80) < DMTTVA (4.94) < DPTTVA (5.25). The log K order is: DMTVA > DMTTVA > DPTTVA > DOTTVA.

It is evident from the order of pK_a values of the acids and that of log K of the complexes that the introduction of a methyl group into the *ortho*, *meta* and *para* positions of N-phenyl ring has no parallel effect on the deprotonation and proton transfer complex formation reactions. Lower stabilities of the proton-transfer complexes are observed in the direction of the general acid-weakening. In the proton-transfer complex formation, the steric effects seen to be more significant than the π-interactions operative in the deprotonation processes. The maximum steric hindrance is present in the *ortho*-tolyl derivative. Evidently, here field effects superimpose on steric effects.

On the bases of the UV-visible and IR spectra of DMTVA, DOTTVA, DMTTVA and DPTTVA and their complexes with amines, it is concluded that the tautomeric form II takes part in proton transfer complex formation. A band observed at 1548-1542 cm^{-1} in these acids, characteristic of C-N=O group, become stronger and sharper in complexes of acids with amines. The complexes also show a sharp signal at 1667-1662 cm^{-1} characteristic of C=C group present in tautomer [II]. These are clear indication that the structure [II] actually participates in proton transfer complex formation with amines. Based on the IR data, the proton transfer complex may be assigned the structure [III].



where R –CH_3, O$^-$, m$^-$, p$^-$ (CH_3) C_6H_4 groups

The strength of interaction with amines decreases in the order, tertiary > secondary > primary, with the same alkyl group. With increasing number of carbon atoms, the trend in the variation of the complex stability is quite different and difficult to rationalize. Lack of correlation between pK_b of the amines and log K of the complexes implies that it is the donor molecule which alone determines the extent and structures of proton-transfer interaction.

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