IONIZATION OF ORGANIC COMPOUNDS

V. THIOLACTAMS IN SULPHURIC ACID

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ABSTRACT

The ionization in aqueous sulphuric acid of thiolactams consisting of five-, six-, and sevenmembered rings has been studied. With increasing concentration of acid the ionization ratio increases more rapidly than h_0 . A possible explanation involving the hydration of the thiolactam is given. Changes in the basicity of thiolactams with ring size parallel changes previously found for lactams.

By analogy with the resonance structures of simple amides (1), the structure of lactams (I; X = O) would be expected to be made up by a 60% contribution from structure Ia (X = O) and 40% contribution from structure Ib (X = O), although the relative weights of the contributions could be altered somewhat by ring strain (2). Thiolactams (I; X = S) have higher dipole moments (3), and so should be represented to a preponderant extent by the dipolar form Ib (X = S). The high polarity of the thiolactams (I; X = S, n = 3, 4, and 5) may in part account for the fact that they are solids at room temperature while the corresponding lactams (I; X = O, n = 3, 4, and 5) are liquid, and that (as postulated later in this paper) they appear to be more extensively hydrated in aqueous solution than are the lactams.

It is probable that lactams and thiolactams in strong acid are protonated on the oxygen or sulphur atom to give the conjugate acids (II; X = O or S) (4). Consequently it became of interest to compare the basicities of the two classes of compounds. It seemed



possible that in spite of the greater intrinsic basicity of oxygen as compared with sulphur (cf. OH⁻ and SH⁻), the greater negative charge on the sulphur of thiolactams would cause them to be more basic than lactams. We have accordingly determined the protonation constants of the thiolactams (I; X = S, n = 3, 4, and 5) for comparison with the protonation constants reported for the lactams (I; X = O, n = 3, 4, and 5) (2).

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EXPERIMENTAL

Materials

Piperidone (I; X = O, n = 4) and caprolactam (I; X = O, n = 5) were prepared in 38% and 67% yields, respectively, by Cornforth, Hunter, and Popjak's modification (5) of the Schmidt reaction. Pyrrolidone (I; X = O, n = 3) was a commercial product. Thiolactams were prepared from these lactams by treatment with phosphorus pentasulphide following the procedure of Tafel and Lawaczeck (6), and recrystallized to constant (though not necessarily sharp) melting point: thiopyrrolidone from water, m.p. 110–114° (lit. m.p. 116° (6)); thiopiperidone from aqueous ethanol, m.p. 94–95° (lit. m.p. 93–94° (7)); and thiocaprolactam from aqueous ethanol, m.p. 105–107° (lit. m.p. 105–105.5° (7)).

Sulphuric acid solutions were prepared and standardized as described previously (8).

Procedure

Apparatus and procedure were essentially as described before (9), except that thiocaprolactam, because of its insolubility in water, was dissolved in ethanol to make up a stock solution. Aliquots (1.00 ml) of this stock solution were diluted with aqueous sulphuric acid to 50.0 ml, so that the thiocaprolactam solutions contained about 2% (v/v) ethanol. No account was taken of this content of the ethanol in calculations of the H_0 values of the solutions; this seems reasonable from data in the literature (10).

RESULTS AND DISCUSSION

The absorption spectra of thiolactams in aqueous solution (Table I) show a strong peak at about 260 m μ due to a $n \rightarrow \sigma^*$ transition (11), and a second peak at about

TABLE I Absorption peaks of thiolactams

Compound	In water		In sulphuric acid		
	$\lambda_{\max} (m\mu)$	ε _{max}	Concn. (%)	$\lambda_{max} (m\mu)$	ϵ_{\max}
Thiopyrrolidone	$211 \\ 260$	5,860 14 400	78.8	234	10,200
Thiopiperidone	$\begin{array}{c} 200\\ 212\\ 269\end{array}$	5,620	69.4	239.5	9,400
Thiocaprolactam*	$\begin{array}{c} 200\\ 210\\ 271 \end{array}$	5,410 15,100	87.0	243	10,500

*Solutions contained about 2% (v/v) ethanol.

210 m μ which may be due to a $\pi \to \pi^*$ transition, although the assignment is uncertain (11). In strong sulphuric acid these are replaced by a single peak at about 240 m μ (Table I) which may be the $\pi \to \pi^*$ peak shifted to longer wavelengths by protonation (12), the blue shift of the $n \to \sigma^*$ peak (11) caused by protonation having taken it out of the observable region of the spectrum. These spectral changes are very similar to those already observed for thioacetamide (11, 13).

In keeping with the conception that the spectra of the thiolactams in strong acid are due to the monoprotonated species (II), the curves obtained in intermediate concentrations of acid are intermediate in character, and pass through an isobestic point at about 250 m μ and almost through a second isobestic point at about 220 m μ . This is shown for thiopiperidone in Fig. 1. The failure of the curves to pass through the second isobestic point indicates that the peak at lower wavelengths is being shifted by changing acid concentration through a "medium effect" (14).

Plots of the molar extinction coefficients of the thiolactams at a given wavelength against the H_0 values of the acid solutions give sigmoid waves whose inflection points indicate protonation constants (pK_{BH^+}) of -2.0 for thiopyrrolidone, -1.4 for thiopiperidone, and -1.6 for thiocaprolactam. However, as shown in Fig. 2, the curves drawn

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FIG. 1. Ultraviolet absorption of thiopiperidone in the following concentrations of sulphuric acid: a, 0; b, 15.0; c, 20.3; d, 23.0; e, 25.0; f, 27.8; g, 30.5; h, 33.0; i, 38.3; j, 69.4%.



FIG. 2. Ionization of thiolactams in sulphuric acid. Points: experimental values of ϵ for wavelengths (λ) indicated below; curves: calculated from equation [1] using parameters indicated below. (A) Thiopyrrolidone: λ 260 m μ ; p K_{BH^+} -2.0; ϵ_B 14,400; ϵ_{BH^+} 360. (B) Thiopiperidone: λ 269 m μ ; p K_{BH^+} -1.4; ϵ_B 13,050; ϵ_{BH^+} 150. (C) Thiocaprolactam: λ 271 m μ ; p K_{BH^+} -1.6; ϵ_B 15,100; ϵ_{BH^+} 400.

through the experimental points are all slightly steeper in the region of half-ionization than the curves theoretically required by the equation

$$pK_{BH^+} = H_0 - \log \{(\epsilon_{BH^+} - \epsilon)/(\epsilon - \epsilon_B)\}, \qquad [1]$$

 $\epsilon_{\rm B}$, $\epsilon_{\rm BH^+}$, and ϵ being the molar extinction coefficients of the unprotonated base, the protonated base, and the mixture of protonated and unprotonated molecules in a solution of acidity function H_0 , respectively.

Systematic deviation of experimental points from such a theoretical curve has often been attributed to the medium effect (14). However, in the present instance medium effects seem to be absent in the spectral region $240-270 \text{ m}\mu$ as shown by the behavior of the curves in passing through an isobestic point. It seems more probable that we are encountering another class of compounds whose protonation in acid solution does not follow exactly the Hammett H_0 function. It has been shown already that the protonation of amides does not follow this function (9). However, the behavior of amides contrasts with that of thiolactams, in that plots of ϵ against H_0 for the former compounds are *less* steep in the region of half-ionization than required by equation [1].

The contrasting behavior of amides (A) and thiolactams (T) may be explained by postulating that their protonation equilibria (equations [2] and [3]) involve numbers of water molecules (m and p) differing from each other and from the number (n) involved in the protonation of the indicator (In) (equation [4]) used by Hammett (15) for establishing this range of the H_0 scale:

$$AH^+ + mH_2O \rightleftharpoons A + H^+$$
[2]

$$TH^+ + pH_2O \rightleftharpoons T + H^+$$
[3]

$$\ln H^+ + n H_2 O \rightleftharpoons \ln + H^+.$$
[4]

(The formulae in these equations represent hydrated ions or molecules.) If p > n, it can be shown (9) that this requires that the ionization ratio ([TH⁺]/[T]) increase with acid concentration more rapidly than h_0 , and hence that the curve of ϵ against H_0 should be steeper than required by equation [1] at half-neutralization, as was found for thiolactams. On the other hand, if n > m, the ionization ratio ([AH⁺]/[A]) must increase less rapidly than h_0 , and hence the curve of ϵ against H_0 must be less steep than required by equation [1], as was found for amides.

While at the moment it would be difficult to predict that p > n > m, it seems reasonable to expect p > m, because the very polar T should be expected to be more heavily hydrated than the less polar A (1). (AH⁺ and TH⁺, having very similar structures, are expected to be hydrated to approximately the same extent.) Similar considerations probably apply to the hydration of some thioureas, whose ultraviolet absorption changes with acidity in a fashion similar to that shown in Fig. 2 (16).

Thiolactams thus prove to be considerably weaker bases than the corresponding lactams (2), the greater intrinsic basicity of the oxygen atom evidently being more important than the greater negative charge on the sulphur atom. The change in basicity of thiolactams with ring size parallels the charge in basicity of lactams with ring size, as shown in Fig. 3. (In this figure pK_{BH} , values of lactams (2) obtained by the indicator



FIG. 3. Relation of protonation constants of lactams (O, left-hand scale) and of thiolactams (\triangle , right-hand scale) to ring size.

method of Lemaire and Lucas (17) are used.) It is accordingly possible that the reasons given by Huisgen and his co-workers (2) for the variation in basicity of lactams with

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ring size apply also to thiolactams. For the very limited data available the basicities of thiolactams are given with fair precision by the equation

> pK_{BH^+} (thiolactam) = 0.62p K_{BH^+} (lactam) - 1.8. [5]

No simple relationship is discernible between the dipole moments of lactams (18) or thiolactams (3) and their basicities.

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