A Study of the Dimerization of Some Thiolactams

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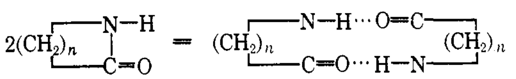
Abstract: The values of $\Delta H°$, $\Delta G°$, and $\Delta S°$ for the dimerization of thiobutyrolactam, thiovalerolactam, and thiocaprolactam have been determined from infrared spectral data. The $\Delta G°$ values indicate that the thio compounds are as highly or more associated than the comparable oxygen compounds, while values of $\Delta H°$ indicate that the N—H···S=C bond is weaker than the N—H···O=C bond in the analogous molecules. The high association of the thio compounds can be justified on the basis of the entropy factor. The relative strengths of the hydrogen bonds are discussed in terms of the acidity and basicity of the thiolactams and lactams.

During the past few years a good deal of attention has been paid to the association of amides and to the hydrogen bonds formed in this association.[1] In the case of cyclic amides (lactams) this association has been fairly easy to study since the evidence indicates that in dilute solutions the predominant species present are monomers and cyclic dimers.[2-5] For these lactams, infrared data were used to determine the equilibrium constants (K_d) and $\Delta H°$'s for the reaction



(1)

where n = 3, 4, and 5.

In contrast to the amides, H bonding in thioamides has not been studied to any great extent. Both cryoscopic[6] and infrared[7-9] data have been interpreted as indicating the formation of N—H···S=C bonds. However, there is very little quantitative data indicating the strength of this interaction. In this paper we present the results of an infrared spectral study of dilute solutions of thiolactams in CCl_4. Values of the dimerization constants and other thermodynamic constants calculated from absorbance data are compared with the values previously determined for lactams.

Experimental Section

Materials. The thiolactams were prepared from the corresponding lactams according to the method given by Tafel and Lawaczeck.[10] These compounds were purified by recrystallizing from ethanol until they had a constant melting point. Mallinckrodt spectral grade CCl_4 was used as the solvent without any further treatment.

Preparation of Solutions. Stock solutions of the thiolactams were prepared by weighing both solute and solvent. The solutions to be used in the experiments were then prepared by quantitative dilutions of the stock solution. These solutions had concentrations in the range of 1×10^{-4} to 8×10^{-4} *M*. The concentration, in moles/liter, at the different temperatures could be calculated by assuming that at these low concentrations the density of CCl_4 and of the solution were the same. All solutions were used within a few hours after preparation.

Spectral Measurements. All spectra were recorded on a Perkin-Elmer 112 single beam, double-pass spectrophotometer. The instrument was equipped with a CaF_2 prism. The cells had a path length of 10 cm, and the optical faces were NIR transmitting quartz. Temperature control of the cell was obtained by using a special aluminum cell holder through which water at a constant temperature was passed. The absorbance of the solution was determined employing the pure solvent as a blank.

Calculations. The treatment developed by Lord and Porro[2] for studying the dimerization of caprolactam is equally applicable to the study of thiolactams provided the following assumptions are valid. The equilibrium involves only monomer and cyclic dimer. Beer's law is valid for the monomer, and the dimer does not contribute to the absorbance at the monomer peak. With these assumptions, the following equations can be derived.

$$A = \frac{a_m^2 l^2}{2K_d}\left(\frac{C_0}{A}\right) - \frac{a_m l}{2K_d} \tag{2}$$

$$\begin{aligned} \text{slope} \quad m &= a_m^2 l^2/2K_d \\ \text{intercept} \quad b &= -a_m l/2K_d \end{aligned} \tag{3}$$

$$K_d = \frac{m}{2b^2} \tag{4}$$

In these equations A is the absorbance at the monomer peak, C_0 the formal concentration of monomer, l the path length, K_d the equilibrium constant, and a_m the molar absorption coefficient of the monomer.

The slope and intercept were calculated from a least-squares treatment of A *vs.* C_0/A, and K_d was calculated according to eq 4. The value of $\Delta H°$ was then obtained from a least-squares treatment of ln K_d *vs.* $1/T$. The error limits placed on both $\Delta H°$ and K_d were obtained from a standard error treatment.

As a preliminary check on the procedure, the value of K_d for butyrolactam at 25° was measured. The result of this measurement was within 10% of the literature value.[4,11]

Results

The absorption spectra of the four-, five-, and six-membered cyclic thioamides have two peaks in the range 3100 to 3500 cm^{-1}. The positions of these peaks and those of the corresponding lactams are given in Table I. The higher frequency bands in the lactams

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(2) R. C. Lord and T. J. Porro, *Z. Elektrochem.*, **64**, 672 (1960).

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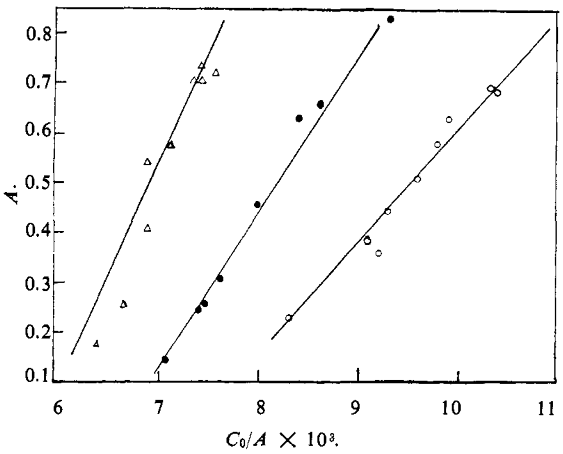

Figure 1. A *vs.* C_0/A for thiolactam dimerization: △, thiobutyrolactam; ●, thiovalerolactam; ○, thiocaprolactam.

have previously been assigned to the N–H vibrations of the free lactams while the lower frequency peaks were assigned to the N–H vibrations in the dimer.[2–5] Since, for each thiolactam, the higher peak is very sharp while the lower peak is quite broad, and the frequencies of the peaks in analogous lactams and thiolactams are very close, it is reasonable to again assign the higher peak to the monomer and the lower peak to the dimer.

Table I. N–H Stretching Frequencies (cm^{-1}) in Thiolactams and Lactams

Name	Monomer	Dimer
Thiobutyrolactam[a]	3440	3225
Butyrolactam[b]	3480	3230
Thiovalerolactam[a]	3390	3177
Valerolactam[c]	3424	3215
Thiocaprolactam[a]	3410	3196
Caprolactam[d]	3430	3217

[a] This work. [b] Reference 4. [c] Reference 3. [d] Reference 2.

The frequencies of the maximum for the two peaks in the thiolactams were found to be independent of both temperature and concentration. This would indicate that, within the temperature and concentration ranges used in these experiments, the equilibrium involves only the monomer and one polymer, the cyclic dimer. Under these circumstances, Lord and Porro's treatment (eq 2-4) is valid. It should be pointed out here that Vinogradov,[12] using Lord and Porro's data, has shown that in dilute caprolactam solutions there is also a small amount of an open-chain dimer which also absorbs at the monomer frequency. The results of this refined calculation indicate that the value of K_d given by Lord and Porro should be changed by 10%. Since the values of K_d reported here have standard deviations in the order of 10%, it is unlikely that the existence of open chain thiolactam dimers and a contribution from the dimer to the absorbance would seriously affect any conclusions drawn from these data. Plots of A *vs.* C_0/A at 25° for each of the thiolactams are shown in Figure 1. In Table II the values of K_d obtained from such plots for each thiolactam at several temperatures are given. The values of $\Delta H°$ obtained from plots of ln K_d *vs.* $1/T$ and the other thermodynamic values of interest are given in Table III. For purposes of comparison, thermodynamic values are also included for the comparable lactams.

Table II. Equilibrium Constants, $K_d = M^{-1}$, for Dimerization of Thiolactams[a]

Temp, °C	Thiobutyrolactam	Thiovalerolactam	Thiocaprolactam
10	585	525	540
15	423	473	505
20	343	504	423
25	278	438	370
30	230	359	338
35	227	329	325

[a] Standard error = 10%.

Table III. Thermodynamic Functions for Dimerization of Thiolactams and Lactams

Name	$\Delta H°$, kcal/mole	$\Delta G°_{25}$, kcal/mole	$\Delta S°$, eu
Thiobutyrolactam[a]	−5.8 ± 0.7	−3.34 ± 0.06	−8.3
Butyrolactam[b]	−7.0 ± 0.4	−3.32	−12.3
Thiovalerolactam[a]	−3.1 ± 0.4	−3.62 ± 0.06	+1.7
Valerolactam[c]	−10.3 ± 1.0	−3.34	−23.4
Thiocaprolactam[a]	−3.9 ± 0.5	−3.52 ± 0.06	−1.6
Caprolactam[d]	−5.5 ± 0.3	−2.77	−9.2

[a] This work. [b] Reference 4. [c] Reference 3. [d] Reference 2.

Discussion

Previously, comparisons of the dimerization of molecules in which sulfur had been substituted for oxygen indicated that, when a thiol group was involved, the association was considerably less than in the analogous oxygen compound.[13,14] For the compounds studied in our work, the substitution involves a thiocarbonyl group which is a better electron donor than the thiol group. Therefore, it might be expected that the differences between the dimerization of thiolactams and lactams would be smaller than the differences observed on thiol substitution, and the values of $\Delta H°$ given in Table III confirm this. Thus, while thiolactams form weaker H bonds than the corresponding lactams, there is still a fair amount of energy per mole of H bonds in the dimers.

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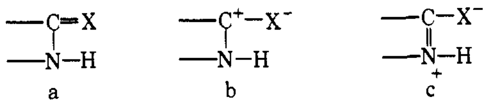
For a further discussion of the factors influencing the strength of the H bonds in these species, it is instructive to examine the resonance structures which can be written for amides and thioamides



where X is a sulfur or oxygen. It is expected that since sulfur is larger than oxygen, the overlap of p orbitals with carbon would not be as great, and resonance forms b and c might have the higher contribution when X is sulfur even though oxygen is the more electronegative atom. Evidence for this being the case has been obtained from the relative dipole moments of lactams and thiolactams,[15] relative rotational barriers for amides and thioamides,[16] the ultraviolet spectra of thioamides,[17] and the infrared spectra of thioamides.[18] The effect of higher contributions from b and c should be to make the thiocarbonyl group more basic, the NH group more acidic, and the thiolactams form stronger H-bonded dimers than the comparable lactams. However, Edward and Stollar have shown that the five-, six-, and seven-membered cyclic thioamides are much less basic than the similar lactams.[19] This could be explained on the basis of the small size of the oxygen and consequent high electron density more than compensating for the higher charge on the sulfur. In comparing the acidity of the two series, such an effect should not arise since N–H is the acidic group in both cases. In agreement with this, it has been shown that the thio compound is the more acidic when a comparison is made of the two unsaturated systems, 2-pyridone and 2-pyridthione.[20] Thus, it is apparent that while the interamide H bond is weaker in thiolactams because of the lower basicity of sulfur, it is not a great deal weaker because the higher acidity of the N–H group in thioamides partially compensates for the trend in base strength.

From the data given in Table III it can also be noticed that even though the thio compounds from slightly weaker H bonds, the values of $\Delta G°_{25}$ indicate that thiovalerolactam and thiocaprolactam have a higher degree of association than the similar oxygen compounds. This is obviously due to the less negative values of $\Delta S°$ for the dimerization of the thiolactams. This is quite reasonable since the dimers of the thio compounds in comparison to the lactams should have larger $S°$ values because the weaker H bonds allow greater vibrational contributions to the entropy. The $\Delta S°$ difference between thiobutyrolactam and thiovalerolactam (10 eu) seems rather large and can be only partially accounted for by the experimental error.

Separate consideration of $\Delta H°$ and $\Delta S°$ also provides a plausible rationalization for the dimerization data recently presented for 2-pyridone and 2-pyridthione.[21] The values of K_d determined for these compounds from vapor pressure osmometric data have a large amount of scatter. However, they do seem to indicate the opposite trend to that observed for the saturated molecules. It is likely that contributions from resonance forms involving double bonds within the rings increase the charges on nitrogen and the oxygen or sulfur atoms and cause the unsaturated systems to be both more acidic and more basic than the unsaturated compounds. In such a case, the stronger H bonds which then might be expected for the unsaturated compounds would decrease the importance of the entropy in determining K_d, and the trend of $\Delta H°$ would make the unsaturated oxygen compound more associated than the analogous sulfur compound. Also, if both unsaturated compounds have stronger H bonds than the saturated ones, then the $\Delta S°$ values for these compounds would be more nearly equivalent since vibrational contributions to $S°$ of the dimers would be low for both the oxygen and sulfur cases.

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