

The energy of the transition state may be decreased by the formation of six-membered ring (I). This second-order dependence with alkoxide has been observed in the Meerwein-Ponndorf reduction with aluminum alkoxide.⁹

The retardation observed by the addition of benzoyl peroxide or hydrogen peroxide may be due to the suppression of hydrogen atom transfer; the acceleration by the addition of 9-fluorenone implies its role as a hydrogen atom carrier. The role of

(7) V. Tischenko, *J. Russ. Phys. Chem. Soc.*, **38**, 355 (1906); *Chem. Zentr.*, II, 1310 (1906).

(8) L. Claisen, *Ber.*, **20**, 646 (1887).

(9) W. N. Noulton, R. E. Van Atta, and R. R. Ruch, *J. Org. Chem.*, **26**, 290 (1961).

9-fluorenone as a hydride-ion carrier¹⁰ is less probable because of the observed retardation of the reaction on addition of peroxides. Our observation that the addition of benzoquinone or hydroquinone could not produce the retardation may be due to their easy transformation into black amorphous oxidation products in the present reaction mixture.

The tendency of an electron-withdrawing group in nitrobenzene to accelerate the reaction coincides with the above nucleophilic attack of sodium methoxide molecule on the nitrogen atom of nitrobenzene.

(10) A. A. Sayigh, *ibid.*, **25**, 1707 (1960).

The Dipole Moment and Structure of Thiolactams

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Measurement of the dipole moments of thiolactams in dioxane at 30° gives the following: thiopyrrolidone I, 5.07 D; thiopiperidone II, 5.15 D, and thiocaprolactam III, 4.83 D. Comparison of the moments of I, II, and III with the moments of corresponding lactams shows that the thiolactams have dipole moments about 1.0–1.3 D. higher. This is due to the greater inherent polarization of the thiocarbonyl group which is also indicated by the lower infrared stretching frequency and the lower maxima and greater extinction in the ultraviolet. These data indicate that there is more of the ionic form $\overset{+}{C}-\overset{-}{X}$ (X = S or O) present in thiolactams than in lactams.

Sulfur and oxygen are isoelectric, *i.e.*, in their outermost shell they both have two *s* and four *p* electrons. Both sulfur and oxygen would thus be expected to be capable of forming two single or one double bond.

Sanderson¹ has pointed out the major differences that affect the chemistry of the two elements. The kernel of ten electrons in sulfur compared to only two electrons in oxygen makes sulfur more likely to form single bonds than multiple bonds. The greater size of the covalent radii of sulfur compared to oxygen (1.02 Å. compared to 0.73 Å.) causes the electronegativity of sulfur to be less than oxygen (2.5 compared with 3.5²). Another difference is the ability, completely absent in oxygen atoms, of sulfur atoms to utilize its outer 3 *d* orbitals.

These differences would be expected to have a pronounced effect on the electronic distribution of thiolactams compared with lactams. This difference is reflected in the dipole moments, infrared and ultraviolet spectra of the thiolactams.

Results and Discussion

Table I gives the dipole moments of thiopyrrolidone I, thiopiperidone II, and thiocaprolactam III in dioxane at 30° along with the previously

determined moments of the carbonyl analogs. In all three cases, the moments of the thiolactams are higher than those of the corresponding lactams.

The lower electronegativity of sulfur compared

TABLE I

DIPOLE MOMENT OF THIOACTAMS AND LACTAMS IN DIOXANE AT 30° AND INFRARED THIOCARBONYL AND CARBONYL FREQUENCIES^a

	5.07 D	3.79 D
I. Thiopyrrolidone	1115 cm. ⁻¹	Pyrrolidone ^b 1706 cm. ⁻¹
	5.15 D	3.83 D
II. Thiopiperidone	1112 cm. ⁻¹	Piperidone ^c (benzene 25°) 1672 cm. ⁻¹
	4.83 D	3.88 D
III. Thiocaprolactam	1117 cm. ⁻¹	Caprolactam ^{c,d} (benzene 25°) 1669 cm. ⁻¹
Moment of thiolactam minus moment of lactam		1.28 D 1.32 D 0.95 D

^a See ref. 9. ^b See ref. 10. ^c See ref. 11. ^d See ref. 12.

to oxygen might have been expected to cause a decrease in the moment of the thiolactam com-

(1) R. T. Sanderson, "Chemical Periodicity," Reinhold, New York, 1960, p. 208.

(2) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, 1960, p. 90.

pared with the carbonyl compound. Mautner and co-workers³⁻⁵ have shown that the dipole moment of the thiocarbonyl compounds is always greater than the corresponding carbonyl analogs. They attribute this to a greater *inherent* contribution of the ionic form $\overset{+}{\text{C}}-\overset{-}{\text{S}}$ in the thiocarbonyl group than for the $\overset{+}{\text{C}}-\overset{-}{\text{O}}$ form in the carbonyl group. Spectral and other data confirm this.

Smyth^{6,7} gives the bond moments of the carbonyl group as 2.3 D and the thiocarbonyl group as 2.6 D, a difference of 0.3 D. Kumler and Fohlen⁸ measured the dipole moments of urea and thiourea in dioxane at 25° and obtained values of 4.56 D and 4.89 D, respectively. The higher moment of urea and thiourea over simple amides is due to the fact that there are two equivalent forms with a separation of charge that contribute to the ureide structure.

The difference in the moments of thioactams I, II, and III and their oxygen analogs is in the order of 1.0 to 1.3 D, higher than the theoretical 0.2-0.3 D. Lactams, like monosubstituted ureas, do not have two equivalent resonance structures (which would increase their moment) and the greater polarization of the thiocarbonyl group gives a higher moment for the sulfur compound. The dipole data indicates that there is more of the ionic form $\overset{+}{\text{C}}-\overset{-}{\text{X}}$ (X = S or O) present in thioactams than in lactams.

Infrared Data.—Since the dipole data indicates that the thiocarbonyl group has more single bond or ionic character than the carbonyl group, one would expect this to show up in the infrared spectra. Studies on the thiocarbonyl stretching frequency¹³⁻¹⁷ show this is so.

One would predict that the force constant of the thiocarbonyl group would be less than the force constant of the carbonyl group because of the greater single bond character in the former group. This would lead to a lower frequency for the thiocarbonyl stretching mode than for the carbonyl

group because of the lesser energy required for oscillation. The greater single bond character in the thiocarbonyl group is reflected in the bond lengths of the two groups. The carbonyl bond length is 77.0% of the single covalent bond, while the thiocarbonyl bond length is 88.5% of the single covalent bond.¹⁸ Mecke¹⁵ calculated that the $\nu_{\text{C=O}}/\nu_{\text{C=S}}$ would be around 1.5 so the $\nu_{\text{C=S}}$ would be about (1800-1560)/1.5 or 1200-1050 cm^{-1} . Strong absorption near 1120 cm^{-1} has been shown for the three thioactams¹⁶ (Table I). (Our values for these compounds in potassium bromide are 1110 to 1111 cm^{-1} .) The thiocarbonyl stretching frequency is not as sensitive to polar effects as the carbonyl group.¹⁶ There is only a difference of 5 cm^{-1} between the three thioactams, while the three lactams show a difference of 37 cm^{-1} . Although there is not a linear relationship, the higher the dipole moment (more of the ionic form or greater single bond character) the lower the thiocarbonyl and carbonyl frequency. The fingerprint region of the three thioactams show appreciable differences.

Ultraviolet Spectra.—Matsen¹⁹ states that aliphatic thiocarbonyl transitions are identical with those of the carbonyl group. The long wavelength absorptions are at lower frequency than the corresponding carbonyl absorption because of the "weaker binding of the γ electrons on sulfur." Ferguson²⁰ gives the following values for various C=X (X = C, N, O, S) ultraviolet transitions:

Compound	λ_{max}
$\text{CH}_2=\text{CH}_2$	180 $\text{m}\mu$
$(\text{CH}_3)_2\text{C}=\text{N}-\text{CH}_3$	230 $\text{m}\mu$
$(\text{CH}_3)_2\text{C}=\text{O}$	280 $\text{m}\mu$
$(\text{CH}_3)_2\text{C}=\text{S}$	400 $\text{m}\mu$

Mautner and Kumler³ give the following values:

	λ_{max}	ϵ_{max}
Phenylurea	238 $\text{m}\mu$	15,600
Phenylthiourea	267 $\text{m}\mu$	10,950

In both cases, the thiocarbonyl group absorbs at a lower frequency than the carbonyl compound.

The ultraviolet data for I, II, and III in ethanol are given below as well as the data for the corresponding lactams.¹¹ As would be predicted,

Ring Size	Thioactams		Lactams	
	λ_{max}	ϵ	λ_{max}	ϵ
5	262 $\text{m}\mu$	14,800	214 $\text{m}\mu$	400
6	274 $\text{m}\mu$	13,200	221 $\text{m}\mu$	400
7	278 $\text{m}\mu$	15,000	223 $\text{m}\mu$	400

the thioactams absorb at a lower frequency (higher wave length) than the carbonyl compounds and have a higher extinction.

The dipole moments, infrared and ultraviolet spectra of the thioactams and Mautner's³⁻⁵

(3) H. G. Mautner and W. D. Kumler, *J. Am. Chem. Soc.*, **78**, 97 (1956).

(4) H. G. Mautner, *ibid.*, **78**, 5292 (1956).

(5) H. G. Mautner and E. M. Clayton, *ibid.*, **81**, 6270 (1959).

(6) C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 183 (1938).

(7) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, 1955, p. 245.

(8) W. D. Kumler and G. M. Fohlen, *J. Am. Chem. Soc.*, **64**, 1944 (1942).

(9) All infrared frequencies from ref. 16.

(10) C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4593 (1961).

(11) R. Huisgen, *Angew. Chem.*, **69**, 341 (1957); R. Huisgen and H. Walz, *Chem. Ber.*, **89**, 2616 (1956).

(12) N. Ogata, *Bull. Chem. Soc. Japan*, **32**, 813 (1959).

(13) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen, London, 1958, pp. 355-356.

(14) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, p. 3871 (1955).

(15) R. Mecke, Jr., R. Mecke, u. A. Lutbringhaus, *Z. Naturforsch.*, **10B**, 367 (1955).

(16) R. Mecke, Jr., and R. Mecke, *Chem. Ber.*, **89**, 343 (1956).

(17) E. Spinner, *J. Org. Chem.*, **23**, 2037 (1958).

(18) R. T. Sanderson, "Chemical Periodicity," Reinhold, New York, 1950, p. 50.

(19) F. A. Matsen in W. West et al., "Chemical Applications of Spectroscopy," Interscience, N. Y., 1956, p. 663.

(20) L. N. Ferguson, "Electron Structures of Organic Molecules," Prentice Hall, N. Y., 1952, p. 276.

work on other thiocarbonyl compounds show that the thiocarbonyl group is inherently more polarizable. There are a number of reasons for this greater polarizability. The larger kernel of electrons in sulfur compared to oxygen (ten to two) "inhibits the stable *closeness of interaction* characteristic of multiple bond."¹ This "labilization of the ground state" is due to the increased difficulty of forming a π bond as the interatomic distances are increased because of the decreased overlap of the p orbitals.^{3,20} This greater "strain" in the thiocarbonyl group as compared with the carbonyl group (a double bond can be considered a two-membered ring) would make the ionic form $\overset{+}{\text{C}}-\overset{-}{\text{S}}$ more favored.^{20,21} The difference in "strain" shows up in the bond energies for the two groups.²² The bond energy for the C=O group is 152 kg. cal., while that for the C=S group is 103. Twice the C—O bond energy is 140 which is less than 152, indicating the stability of the carbonyl group. Twice the C—S bond energy is 109, which is greater than 103 in accordance with the tendency of thioaldehydes and aliphatic thioketones to trimerize by which carbon-sulfur double bonds are converted to single bonds.

Mautner and Kumler³ have pointed out that the ability of the 3 d orbitals in sulfur to accept electrons may stabilize the activated state $\overset{+}{\text{C}}-\overset{-}{\text{S}}$.

So, in spite of the lower electronegativity of sulfur compared with oxygen, the "labilization of the ground state" due to "strain" in the thiocarbonyl group and the stabilization of the activated state though the acceptance of electrons in 3 d orbitals increases the polarizability of the thiocarbonyl group over that of the carbonyl group.

Experimental

Thiolactams I, II, and III were measured in dioxane at 30° and calculations were made using the equation and method of Halverstadt and Kumler.²³

TABLE II
DIPOLE MOMENTS OF THIOACTAMS IN DIOXANE AT 30°

	ϵ_{11}	ϵ_{12}	ϵ_{22}
I. Thiopyrrolidone			
	0.0010374	2.23176	0.97850
	.0015086	2.24571	.97843
	.0020206	2.26166	.97834
μ 5.07 \pm 0.02 D	.0028914	2.28885	.97819
	.0035266	2.30907	.97812
ϵ_1 2.19904 ν_1 0.97867 P_{20} 546.26			Mol. wt. 101.12
α 31.11948 β -0.16500 P_E 30.75 calcd.			
II. Thiopiperidone			
	0.0008913	2.22496	0.97816
	.0014555	2.24179	.97809
	.0017249	2.24876	.97803
	.0023826	2.26732	.97799
	.0027544	2.27778	.97794
μ 5.15 \pm 0.02 D	.0034090	2.29635	.97788
ϵ_1 2.20015 ν_1 0.97825 P_{20} 569.05			Mol. wt. 115.14
α 28.2175 β -0.11072 P_E 36.62 calcd.			
III. Thiocaprolactam			
	0.00	2.21877	0.97450
	.0050201	2.33296	.97384
	.0066846	2.37191	.97363
	.0091243	2.42036	.97341
μ 4.83 \pm 0.03 D	.0101580	2.44578	.97319
	.0123288	2.49868	.97286
ϵ_1 2.21920 ν_1 0.97451 P_{20} 508.06			Mol. wt. 129.14
α 22.46901 β -0.12962 P_E 39.92 calcd.			

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(21) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 282 (1939).

(22) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Chemical Publishing Co., New York, 1960, p. 169.

(23) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).