

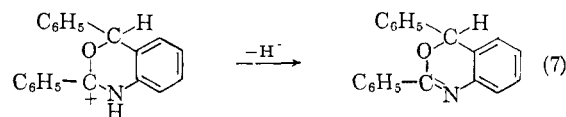
of the α -bromotoluic acids are now regarded as special cases (see eq. 4 and 5), and the thermodynamic constants reported for these compounds will not be discussed until further work on their hydrolyses has been done. For the other reactions, except for those of the carbophenoxybenzhydryl bromides, the activation energies for the *o*-isomers are equal to or greater than those for the corresponding *p*-isomers. In the case of the carbophenoxybenzhydryl halides the E_a value for the *o*-isomer is 3.5 kcal. less than that for the *p*-isomer, a differential which is considered to reflect the energetic advantage of reaction in the presence of a participating substituent. The activation entropy for the *ortho* compound is more negative than that for the *para* compound, whereas in most cases the reverse is true. Where *ortho* participation does not occur, it is probable that the entropy losses attending solvation in the transition state are, because of steric hindrance to solvation, less than those for the *p*-isomers. The fact that the entropy of activation for reaction of *o*-benzoyloxybenzhydryl bromide is more negative than that for the *p*-isomer cannot be taken as evidence of *o*-substituent participation, since such participation clearly does not occur in the hydrolysis of *o*-benzoyloxybenzhydryl bromide.

The Attempted Preparation and Hydrolysis of *o*-Benzamidobenzhydryl Bromide.—As described in the Experimental section a pure sample of *o*-benzamidobenzhydryl bromide, a compound potentially subject to hydrolysis *via* an intramolecular nucleophile-catalyzed process, could not be prepared. The crude product obtained by gassing *o*-benzamidobenzhydryl bromide was subjected to hydrolysis in 90% aqueous acetone in an attempt both to estimate the reaction rate and to characterize the bromide in terms of the structure of its hydrolysis product. The material isolated from the reaction in aqueous acetone, which is presumed to be 2,4-

TABLE VI
THE HEAT AND ENTROPY OF ACTIVATION FOR THE HYDROLYSIS OF THE BROMIDES

| X | E_a , kcal./mole | $-\Delta S^\ddagger$, e.u. |
|--|-----------------------|--------------------------------|
| XC ₆ H ₄ CH ₂ Br in 80% aq. dioxane | | |
| H | 19.4 ± 0.4 | 26.1 ± 1.2 |
| <i>o</i> -COOH | 18.5 ± 1.1 | 21.8 ± 3.2 |
| <i>p</i> -COOH | 19.2 ± 0.7 | 28.4 ± 2.0 |
| <i>o</i> -COOCH ₃ | 21.4 ± .6 | 19.7 ± 1.7 |
| <i>p</i> -COOCH ₃ | 17.0 ± .7 | 35.1 ± 2.0 |
| <i>o</i> -OCOC ₆ H ₅ | 19.8 ± .4 | 27.6 ± 1.2 |
| <i>p</i> -OCOC ₆ H ₅ | 20.2 ± .5 | 23.2 ± 1.5 |
| XC ₆ H ₄ CH(C ₆ H ₅)Br in 90% aq. acetone | | |
| H | 18.2 | 16.8 |
| <i>o</i> -OCOCH ₃ | 20.8 ± 0.2 | 12.1 ± 0.7 |
| <i>p</i> -OCOCH ₃ | 18.6 ± .8 | 13.7 ± 2.7 |
| <i>o</i> -OCOC ₆ H ₅ | 21.6 ± .2 | 11.7 ± 0.7 |
| <i>p</i> -OCOC ₆ H ₅ | 18.1 ± .7 | 16.1 ± 2.3 |
| <i>o</i> -COOC ₆ H ₅ | 17.7 ± .4 | 18.8 ± 1.3 |
| <i>p</i> -COOC ₆ H ₅ | 21.2 ± .2 | 16.1 ± 0.7 |

diphenyl - 3,1,4 - benzoxazine, very possibly was formed from the crude bromide *via* a cyclic intermediate (eq. 7). Indications are that hydrolysis



of the *o*-benzamido derivative occurs very rapidly. In view of the uncertainty concerning the identity of the bromide, however, no unqualified statements can be made concerning the course of the reactions leading to the formation of the substituted benzoxazine.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS]

Molecular Complexes and their Spectra. XIV. Iodine Complexes with Thiourea and Thioacetamide

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Spectrophotometric studies of dichloromethane solutions of iodine with thiourea, and with thioacetamide, have shown the existence, in each case, of a new intense absorption band in the near ultraviolet. This band has been interpreted as the charge transfer (CT) band of a 1:1 molecular complex. The thermodynamic and spectral characteristics of these complexes have been determined. It has been found that electronic absorption bands characteristic of thiourea, and of thioacetamide, are shifted toward shorter wave lengths upon complex formation with iodine, along with the well known "blue shift" of the visible iodine band. A discussion on the nature of the bonding and the electronic spectra in these complexes is given.

Introduction

Iodine is known to form 1:1 molecular complexes in solution with such compounds as aliphatic ethers, sulfides and amines in which the lone pair electrons on the oxygen, sulfur and nitrogen atoms, respectively, act as electron donors toward iodine.¹ Iodine is also known to form 1:1 complexes with

aniline derivatives in which the nitrogen lone pair is in intramolecular resonance with the π electrons of the aromatic ring, which should lead to a decrease in the external donor strength of the nitrogen lone pair. Nevertheless, the nitrogen lone pair has been shown to be the probable coordinating site for iodine in these 1:1 complexes.²

In addition, the existence of 1:1 iodine complexes

(1) H. Tsubomura and R. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961); additional references are cited in this paper.

(2) H. Tsubomura, *ibid.*, **82**, 40 (1960).

with amides has recently been established.^{1,3} Infrared evidence has been presented³ to show that the coordinating site is at the oxygen rather than the nitrogen atom, which is in agreement with some infrared⁴ and nuclear magnetic resonance^{5,6} work on amides complexing with some electron acceptors other than iodine. Thiourea and thioacetamide also provide two possible sites for complexing: the sulfur atom or the nitrogen atom. Thiourea is known to form complexes with most of the transition metals, and in these complexes the coordinating site is believed to be at the sulfur atom.⁷ On the other hand a recent ultraviolet spectrophotometric study of the protonation of thioacetamide in aqueous HCl was interpreted in terms of a proton coordinating with the nitrogen lone pair, resulting in a complex that is isoelectronic with thioacetone.⁸ The present study was undertaken to determine the thermodynamic and spectroscopic characteristics of the possible 1:1 iodine complexes of thiourea and thioacetamide.

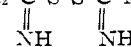
Experimental

Materials.—Fisher Certified iodine was resublimed under reduced pressure. Fisher spectrograde dichloromethane was dried with Drierite and distilled with a Poddelniak column. Eastman White Label thiourea was recrystallized from absolute ethanol and Eastman White Label thioacetamide was recrystallized from absolute ether. Thioacetamide decomposes easily and had to be freshly recrystallized for each series of measurements, which were performed as soon as possible after the recrystallization. Impure thioacetamide has an obnoxious odor, similar to that of impure acetamide, and the 269 $m\mu$ peak decreases with increasing decomposition. Consequently, the odor and the extinction coefficient of the 269 $m\mu$ peak ($\epsilon_{\max} = 12,300$ l. mole⁻¹ cm.⁻¹ in dichloromethane) were employed as criteria for purity of the thioacetamide since the melting point criterion was not sufficient.

Method.—A standard Beckman Model DK-2 Spectrophotometer was employed for all spectroscopic measurements. A pair of matched Beckman one cm. silica "U" rectangular cells was employed for all the spectroscopic measurements. The spectrophotometer was equipped with a Beckman temperature-regulated cell holder, and a constant temperature was maintained by circulating water, at room temperature, through the cell holder. The low temperatures were achieved by circulating water that was cooled to the desired temperature through the cell holder. The temperatures were measured by a thermometer inserted in a thermometer well in the cell holder throughout the course of the spectrophotometric measurements. The temperatures were maintained constant to about $\pm 0.5^\circ$. Because of the low boiling point of dichloromethane, temperatures above room temperature were not employed. The instrument was also equipped with a Beckman purge kit and dry nitrogen was flushed through the cell compartment during the low temperature measurements to prevent condensation of water vapor on the cell windows and other optics located nearby.

Preparation of Solutions.—As in the cases of acetamide and N,N-dimethylformamide,¹ it was found that nonpolar solvents such as *n*-heptane, perfluoroheptane and carbon tetrachloride dissolve very little thiourea and thioacetamide. And as in the case of the amides, chloroform was found to

react slowly with the iodine complexes of thiourea and thioacetamide. It has been reported that thiourea is oxidized by iodine to the disulfide, $\text{NH}_2\text{-C-S-S-C-NH}_2$, in such sol-



vents as water, methanol, ethanol, acetic acid, inorganic acids, neutral buffer solutions, benzene and chloroform.⁹ Thioacetamide is hydrolyzed in aqueous acidic and basic media to form sulfide ion, this being the basis of its use in inorganic qualitative analysis.

Dichloromethane was found to dissolve sufficient amounts of thiourea and thioacetamide so that in solutions with iodine the characteristic "blue shift" of iodine complexes could be observed in the visible and a new, intense absorption band was found in the near ultraviolet. Hence dichloromethane was employed as the solvent for a spectrophotometric study of these complexes. When iodine was dissolved in unpurified dichloromethane, the two bands characteristic of I_3^- appeared at about 290 and 360 $m\mu$, but after purification these two bands completely disappeared. It was observed that upon standing the I_2 completely disappeared when unpurified dichloromethane was used as solvent. In solutions of thiourea and iodine in unpurified solvent the charge transfer band gradually disappeared upon standing, but with the purified solvent the complex was stable for hours without any apparent reaction between thiourea and iodine. It seems that some impurity that reduces I_2 to I^- is required to catalyze the reaction between thiourea and iodine.

Stock solutions of iodine and thioacetamide were prepared by weighing and subsequent dilution to volume in volumetric flasks. The solutions employed for the spectrophotometric measurements were prepared from stock solutions by pipetting the calculated volumes into ten ml. volumetric flasks. All stock solutions were freshly made on the day of measurement because of the low boiling point of dichloromethane.

Thioacetamide was sufficiently soluble in dichloromethane that the concentrations could be determined by weighing. The much smaller solubility of thiourea made this impractical so that the concentrations of thiourea were determined in a different way: they were measured in terms of a saturated solution in dichloromethane. The concentration of thiourea in a saturated solution was determined by first filtering the excess thiourea from a saturated solution. Then a measured volume of this filtered, saturated solution was placed in a vacuum desiccator and the dichloromethane was slowly evaporated off. The dried thiourea was then dissolved in absolute ethanol to the same volume as the original dichloromethane and this solution was measured on the spectrophotometer. Using a previously determined extinction coefficient at the 242 $m\mu$ peak for thiourea in absolute ethanol (determined from a solution having approximately the same concentration as the saturated thiourea solution), the concentration of thiourea in a saturated dichloromethane solution was determined to be $(1.2 \pm 0.1) \times 10^{-3}M$ at room temperature.

Results

The CT Band and the Determination of K (Thiourea).—In Fig. 1 are shown the spectra of three of the solutions employed to determine the equilibrium constant at 22° . The intense absorption band with its peak at 298 $m\mu$ is identified as the charge transfer band of the thiourea-iodine complex and the strong absorption at shorter wave lengths is due to thiourea, which has two intense peaks in the near ultraviolet. The longest wave length peak is at 253 $m\mu$ in dichloromethane (242 $m\mu$ in absolute ethanol) with an ϵ_{\max} of 1.25×10^4 l. mole⁻¹ cm.⁻¹ at 22° , whereas the shorter wave length peak cannot be located in these solutions because dichloromethane begins to absorb strongly below 235 $m\mu$. At the concentrations employed to determine K , iodine has no appreciable absorption at 298 $m\mu$, but there is a small absorption due to thiourea. Because of this small absorption a correction was made for the uncomplexed thiourea.

(9) A. Luttringhaus, *Arzneimittel Forsch.*, **3**, 333 (1953).

(3) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

(4) E. L. Muetterties, *ibid.*, **82**, 1082 (1960).

(5) W. Gerrard, M. F. Lappert, H. Pyzora and J. W. Wallis, *J. Chem. Soc. (London)*, 2144 (1960).

(6) (a) G. Fraenkel and C. Nieman, *Proc. Natl. Acad. Sci. (U. S.)*, **44**, 688 (1958). (b) G. Fraenkel and C. Franconi, *J. Am. Chem. Soc.*, **82**, 4478 (1960).

(7) John C. Bailar (Editor), "The Chemistry of Coordination Compounds," Reinhold Publishing Corporation, New York, N. Y., 1956, p. 53.

(8) H. Hosoya, J. Tanaka and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 850 (1960).

By using the equation for the equilibrium constant for 1:1 complex formation

$$K = \frac{[C]}{([I] - [C])([T] - [C])} \quad (1)$$

and substituting the term A/ϵ for $[C]$ (for a path length of one cm.) the following equation can be derived

$$\frac{[I][T]}{A} = \left([I] + [T] - \frac{A}{\epsilon} \right) \frac{1}{\epsilon} + \frac{1}{K\epsilon} \quad (2)$$

where A is the absorbance due to the complex, $[T]$ is the initial concentration of thiourea, $[I]$ is the initial concentration of iodine, ϵ is the molar extinction coefficient of the complex, and K is the equilibrium constant for 1:1 complex formation. In cases where the initial concentration of the donor is greater than one hundred times the initial concentration of the iodine, the term $([T] - [C])$ reduces to $[T]$ in equation 1. In this case equation 2 reduces to the form

$$\frac{[I][T]}{A} = \frac{[T]}{\epsilon} + \frac{1}{K\epsilon} \quad (3)$$

and a plot of $\frac{[I][T]}{A}$ vs. $[T]$ should yield a straight line of slope $1/\epsilon$ and intercept $1/K\epsilon$. Because the K for the thiourea-iodine complex is so large and, consequently, a sufficient amount of complex is formed without the donor concentration being much greater than the iodine concentration, equation 3 could not be employed. Nevertheless, a plot of $\frac{[I][T]}{A}$ vs.

$\left([I] + [T] - \frac{A}{\epsilon} \right)$ would also yield a straight line with slope $1/\epsilon$ and intercept $1/K\epsilon$. However, a knowledge of the unknown quantity ϵ is needed to make this plot.

Consequently, a tentative value of ϵ is determined by using data from two solutions and solving equation 2 simultaneously for ϵ and K . Using this value of ϵ a plot is made, employing data from a series of solutions, and a new value of ϵ is determined along with a new value of K . This procedure is repeated until a consistent set of values for both ϵ and K have been obtained from two successive plots. In this particular case, only two plots were required to obtain consistent values for ϵ and K . The same procedure was employed with data at three different temperatures. If the data are very good and there is only one form of the complex, and this is of the 1:1 type, then an almost perfect straight line should be obtained. On the other hand, if the data are not too good there will be considerable random scattering of the experimental points from perfect linearity, and these deviations are a measure of the probable uncertainty in the experimentally determined values of K and ϵ .

If the complex being investigated is not 1:1 or the solution contains a mixture of a 1:1 complex and a complex with some other mole ratio, then a plot of equation 2 should not give a straight line. But in order to use this linearity as a criterion for 1:1 complex formation, the experimental data must cover a wide range of donor and acceptor concentrations to be sure that the resulting linearity is not the almost linear portion of a broad curve.

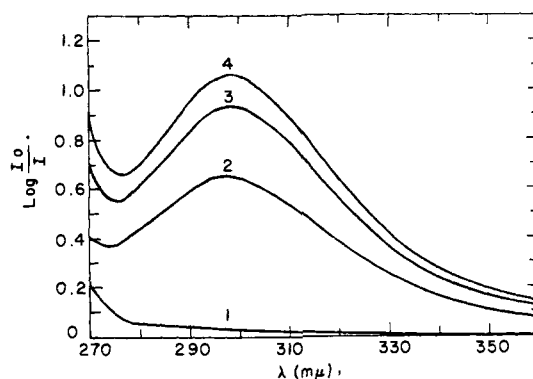


Fig. 1.—The ultraviolet absorption spectra of iodine-thiourea solutions. Solvent, dichloromethane; temperature 22°, cell, 1 cm. Curve 1, $1.2 \times 10^{-4} M$ thiourea; curve 2, $1.2 \times 10^{-4} M$ thiourea and $2.62 \times 10^{-5} M$ iodine; 3, $2.4 \times 10^{-4} M$ thiourea and $2.62 \times 10^{-5} M$ iodine; curve 4, $3.6 \times 10^{-4} M$ thiourea and $2.62 \times 10^{-5} M$ iodine.

In general, experimental conditions such as solubility, absorption by donor or acceptor, reaction, additional complex formation, too strong or too weak absorption by the complex, etc. do not permit a wide range of donor and acceptor concentrations to be investigated spectrophotometrically for complex formation. Consequently, other criteria such as isobestic points and the electronic and geometrical structures of the donor and acceptor species are utilized, in addition to these linear plots, to decide the probable mole ratios of complexes in solution.

In the present research the solutions employed for determining K for the thiourea-iodine complex contained iodine at a concentration of about $0.26 \times 10^{-4} M$, and thiourea was in the range $0.6 \times 10^{-4} M$ to $3.6 \times 10^{-4} M$. These solutions gave experimental points lying on a fairly good straight line. The resulting K 's were 7,900 (22°), 14,000 (12°) and 23,000 (4°). All the K values are in $l. \text{mole}^{-1}$ units. A plot of $\ln K$ vs. $1/T$ gave $\Delta H^0 = -9.6 \text{ kcal./mole}$ from the slope and $\Delta S^0 = -14.7 \text{ e.u.}$ from the intercept. By making an estimate of the uncertainty in the K 's, from the deviations in linearity of the plots, the uncertainty in ΔH^0 was determined to be about one kcal./mole.

The CT Band and the Determination of K (Thioacetamide).—The ultraviolet spectrum of thioacetamide is similar to that of thiourea but shifted to longer wave lengths. [The long wave length peak is at 269 $m\mu$ (ϵ_{max} is 12,300) in dichloromethane and the shorter wave length peak could not be located because of the solvent absorption.] The overlap of the thioacetamide 269 $m\mu$ absorption with the charge transfer band of the complex, which was found to occur at the same wave lengths (near 300 $m\mu$) as for the thiourea-iodine complex, is greater than for the corresponding bands of thiourea. The K for this complex was therefore calculated using the wave length range 320 to 340 $m\mu$ where, at the concentrations employed, there was no appreciable absorption due to either free iodine or thioacetamide (impure thioacetamide has a small absorption in this region). Since the peak of the CT band was now not being employed for the K determination as it was for

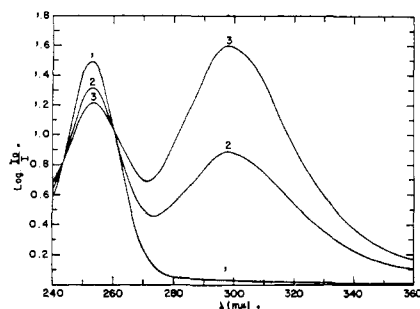


Fig. 2.—The effect of complexing on the ultraviolet spectrum of thiourea. Solvent, dichloromethane; temperature, 24°; cell, 1 cm. Curve 1, 1.2×10^{-4} M thiourea; curve 2, 1.2×10^{-4} M thiourea and 3.72×10^{-5} M iodine; curve 3, 1.2×10^{-4} M thiourea and 7.44×10^{-5} M iodine.

thiourea, the K was evaluated at three wave lengths, using at each the same method as was used for the thiourea-iodine complex. The results of these calculations are tabulated in Table I. In view of the rather large uncertainties in the thermodynamic data a second method was devised to check the physical self-consistency of the interpretation of the K as representing 1:1 complex formation.

TABLE I

THE THERMODYNAMIC AND SPECTRAL CHARACTERISTICS OF THE THIOACETAMIDE-IODINE COMPLEX IN DICHLOROMETHANE

CT band: $\lambda_{\max} = 296 \text{ m}\mu$; $\epsilon_{\max} = \sim 48,000 \text{ l. mole}^{-1} \text{ cm.}^{-1}$. Shifted visible I_2 band^a: $\lambda_{\max} = \sim 400 \text{ m}\mu$; $\epsilon_{\max} = \sim 4,500 \text{ l. mole}^{-1} \text{ cm.}^{-1}$. Shifted thioacetamide band: $\lambda_{\max} = 248 \text{ m}\mu$; $\epsilon_{\max} = \sim 12,000 \text{ l. mole}^{-1} \text{ cm.}^{-1}$.

| K (l. mole ⁻¹) | ϵ (l. mole ⁻¹ cm. ⁻¹) | λ (m μ) |
|------------------------------|---|----------------------|
| 17° | | |
| 11,200 | 25,500 | 320 |
| 12,900 | 17,200 | 330 |
| 12,000 | 12,700 | 340 |
| 12,000 \pm 900 | | |
| 2.5° | | |
| 23,000 | 25,500 | 320 |
| 25,000 | 18,200 | 330 |
| 27,000 | 12,300 | 340 |
| 25,000 \pm 2000 | | |

$$\Delta H^{\circ} = -8.2 \pm 1.8 \text{ kcal./mole}$$

$$\Delta S^{\circ} = -9.5 \pm 6.2 \text{ e.u.}$$

^a Assuming no overlap by the CT band at 400 m μ .

A brief explanation of this method will be presented now. Since the quantity A/ϵ represents the concentration of the complex, this quantity should be constant for any given solution over the wave length range of 320 to 340 m μ . Consequently, by taking the experimental A 's for a given solution at five wave lengths in this spectral region, one should be able to estimate values for the corresponding ϵ 's, by trial and error, such that the quantity A/ϵ should be the same at each of these five wave lengths for this given solution. This set of values for the ϵ 's should also make the quantity A/ϵ constant for the other solutions measured, in this spectral region, if these are the correct ϵ 's. This is essentially a way of determining the best values for the ϵ 's. If all the data were exact, then for any given solution the A/ϵ quantities would be equal for all the wave

lengths considered here. But since experimental data of this kind would not be expected to be exact, there should be small differences between these A/ϵ quantities. Consequently, all the values for A/ϵ for any one solution at various wave lengths are averaged together, and the average value is taken to represent the best value of the concentration of the complex in the given solution. This value is then used to calculate K . This procedure is repeated for all the solutions, and if the data are good all the K 's thus calculated will be nearly identical, and their average can be taken as the best value of K . This method has the advantage that a K can be calculated representing the data for each solution, and any systematic trend in the K 's from solution to solution can be detected. When this method was applied to the thioacetamide-iodine data the K 's were found to scatter randomly from solution to solution with their average value having a 10% maximum deviation, and being within experimental error of the K values obtained by the first method. In addition, essentially the same ϵ values which were calculated by the first method were found to be the best set of values for making the A/ϵ quantities constant in the second method. These results tend to confirm the interpretation of the data as representing 1:1 complex formation.

The Effect of Complex Formation on the Thiourea Spectrum.—The K 's were calculated from solutions in which the iodine concentration was constant and the thiourea concentration varied, since these were found to be the conditions under which the data were least sensitive to experimental error in the K and ϵ determinations using equation 2. In addition, solutions were investigated in which the thiourea concentration was kept constant at 1.2×10^{-4} M and the iodine concentration varied from about 0.4×10^{-4} M to 0.8×10^{-4} M. These conditions permitted the peak of the thiourea band (253 m μ in dichloromethane) to be observed during complex formation. In these solutions (initial thiourea concentration held constant) two absorption peaks could be observed, one at 298 m μ and considered to be the charge transfer band of the complex and the other at 253 m μ , characteristic of thiourea. This situation is shown in Fig. 2.

We observe that as the concentration of the iodine is increased the concentration of the complex also increased, since the intensity of the 298 m μ peak increased, while the intensity of the 253 m μ peak decreased indicating a decrease in the concentration of the uncomplexed thiourea. From the absorbance at 298 m μ and using either the K or ϵ_{\max} value obtained previously, the concentration of the complex could be calculated and subtracted from the initial concentration of thiourea to give that of the free thiourea. Assuming that the 253 m μ absorption was due entirely to free thiourea and using the ϵ_{\max} of the free thiourea, the concentration of free thiourea in equilibrium with the iodine could be calculated independently. It was found, when this was done, that these two values for the concentration of uncomplexed thiourea agreed within the experimental error. This clearly indicated that the 253 m μ absorption is due only to the free thiourea, in equilibrium with iodine and the complex.

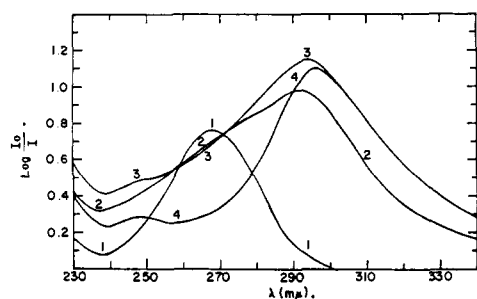


Fig. 3.—The ultraviolet absorption spectra of iodine-thioacetamide solutions. Solvent, dichloromethane; temperature, 17°; cell, 1 cm. Curve 1, $0.62 \times 10^{-4} M$ thioacetamide; curve 2, $0.62 \times 10^{-4} M$ thioacetamide and $0.41 \times 10^{-4} M$ iodine; curve 3, $0.62 \times 10^{-4} M$ thioacetamide and $0.76 \times 10^{-4} M$ iodine; curve 4, solution of curve 3 in sample cell and $0.39 \times 10^{-4} M$ thioacetamide in reference cell.

The spectra of these solutions show two isosbestic points, one on each side of the $253 m\mu$ thiourea peak. The one at $260 m\mu$ is due to the overlap of the $253 m\mu$ thiourea band with the $298 m\mu$ CT band of the complex and indicates the existence of an equilibrium between free thiourea and the complex responsible for the $298 m\mu$ band. This indicates that there is only one form of the complex in equilibrium with thiourea under the experimental conditions employed here. The isosbestic point at $243 m\mu$ should be due to the overlap of the $253 m\mu$ thiourea band with another band characteristic of the complex. This band can be interpreted as a "blue shifted" thiourea band similar to the "blue shifted" visible iodine band. Because of the strong absorption of dichloromethane below $235 m\mu$ and because of the contact charge transfer absorption¹⁰ between iodine and the dichloromethane solvent, which is appreciable below $235 m\mu$, it is impossible to locate the peak of this "blue shifted" thiourea band. The existence of these two isosbestic points strongly suggests that under the conditions studied here there is only one form of the complex in equilibrium with thiourea and iodine. Since these conditions involve the same concentration ranges and ratios of iodine and thiourea as those employed for the K determination, which gave linear plots, and furthermore, since this calculated K quantitatively explained the decrease of the $253 m\mu$ peak upon complex formation, the form of this complex seems to be experimentally substantiated as 1:1.

The Shifted Thioacetamide Band.—Since thioacetamide has its most intense peak at a longer wave length ($269 m\mu$) than that of thiourea, it should be possible to locate the peak of the corresponding "blue shifted" thioacetamide band of the complex. Consequently, solutions were made in which thioacetamide was kept constant at a concentration of about $0.6 \times 10^{-4} M$ and iodine varied from about $0.2 \times 10^{-4} M$ to $0.8 \times 10^{-4} M$. In these solutions two isosbestic points could be detected, one on each side of the $269 m\mu$ thioacetamide peak. These two isosbestic points are located at $271 m\mu$ and $258 m\mu$ and are analogous to those in

(10) L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

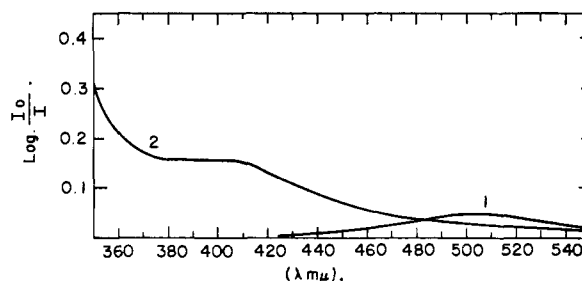


Fig. 4.—The visible absorption spectrum of an iodine-thiourea solution. Solvent, dichloromethane; temperature, 22°; cell, 1 cm. Curve 1, $4.86 \times 10^{-5} M$ iodine; curve 2, $4.86 \times 10^{-5} M$ iodine and $3.6 \times 10^{-4} M$ thiourea.

the thiourea situation which was previously discussed (Fig. 3). In the solution containing $0.62 \times 10^{-4} M$ thioacetamide and $0.76 \times 10^{-4} M$ iodine an inflection could be detected in the spectrum near $250 m\mu$ (curve 3, Fig. 3). Using the previously determined value of K , the concentration of free thioacetamide in this solution could be calculated. When thioacetamide at this calculated concentration was used in the reference cell, to cancel out the absorption due to uncomplexed thioacetamide, the spectrum of the charge transfer band could be obtained (since iodine has no appreciable absorption in this region at the concentration employed here) and showed a peak at $296 m\mu$ with ϵ_{\max} of about 48,000 and ϵ 's in the 320 to $340 m\mu$ range that were essentially the same as those obtained during the K determinations. In addition, a peak could be observed at $248 m\mu$ which can be attributed to the "blue shifted" $269 m\mu$ thioacetamide band (curve 4, Fig. 3). By subtracting off the very small iodine absorption component of this solution, in this wave length region of the shifted thioacetamide band, the ϵ_{\max} was determined to be about 12,000, essentially the same as for the $269 m\mu$ band of free thioacetamide.

The Shifted Visible Iodine Band.—Figure 4 shows the visible spectrum of the thiourea-iodine complex. The spectrum of the initial uncomplexed iodine is included for comparison. The visible spectrum of the complex consists of an increasing absorption leading to a plateau commencing at about $400 m\mu$ and terminating at about $380 m\mu$ with an increasing absorption at shorter wave lengths going to the $298 m\mu$ peak in the near ultra-

TABLE II
THE SPECTRAL CHARACTERISTICS OF THE THIOUREA-IODINE COMPLEX IN DICHLOROMETHANE

| | |
|---|---------------|
| K (20°) (l. mole ⁻¹) | 8,500 |
| $-\Delta H^\circ$ (kcal./mole) | 9.6 ± 1.0 |
| CT band | |
| $\lambda_{\max.}$ (m μ) | 298 |
| $\epsilon_{\max.}$ (l. mole ⁻¹ cm. ⁻¹) | 52,000 |
| $\Delta\bar{\nu}_{1/2}$ (cm. ⁻¹) | 5,400 |
| f | 1.2 |
| D (Debyes) | 8.75 |
| Shifted visible I ₂ band ^a | |
| $\lambda_{\max.}$ (m μ) | 400 |
| $\epsilon_{\max.}$ (l. mole ⁻¹ cm. ⁻¹) | 4,200 |

^a Assuming no overlap by the CT band at $400 m\mu$.

violet. This plateau is due to the superposition of two bands characteristic of the complex, the charge transfer band and the shifted visible iodine band. There seemed to be no way to separate these two bands accurately. Since the plateau starts at 400 $m\mu$, this wave length probably is close to the peak of the shifted visible iodine band. The extinction coefficient of the thiourea-iodine complex at 400 $m\mu$ is given in Table II. The rather large value, which is larger than that of the peak of the shifted visible iodine band for any known iodine complex, seems to indicate that there is considerable overlapping by the CT band at this wave length and that the actual peak is located at a somewhat longer wave length so that this value for ϵ should not be regarded as characteristic of the shifted visible iodine band when resolved from the charge transfer band.

The visible spectrum of the thioacetamide-iodine complex was found to be very similar to that of thiourea and contained a plateau commencing about 400 $m\mu$. The extinction coefficient at this wave length is given in Table I and indicates, in analogy with thiourea, that the actual shifted visible iodine band peak is probably located at a somewhat longer wave length. Free thioacetamide in dichloromethane has a third band with a peak at 356 $m\mu$ and ϵ_{\max} of about 37 l. mole⁻¹ cm.⁻¹. [No analogous band could be detected for free thiourea, either in dichloromethane or water.] This band has been interpreted as probably due to an n to π^* transition involving the sulfur lone pair electrons.⁸ In aqueous solutions this band is overlapped by the tail of the intense 261 $m\mu$ band (269 $m\mu$ in dichloromethane), and its peak was estimated as being at about 318 $m\mu$ with an ϵ_{\max} of about 60. The large "blue shift" of this band (38 $m\mu$) in going from dichloromethane to water as a solvent can be interpreted as due to a resonance stabilization of the sulfur lone pair due to hydrogen bonding with the water molecules since these changes in λ_{\max} and ϵ_{\max} are similar to those attributed to other n to π^* transitions in hydrogen bonding solvents.¹¹

Because of the 356 $m\mu$ absorption the plateau begins to slope upward, toward shorter wave lengths, with increasing thioacetamide concentrations. For solutions with constant iodine concentration an isobestic point was found at about 470 $m\mu$. This isobestic point is due to the overlap of the free and shifted visible iodine bands and indicates that iodine is involved in only one form of complex formation. The solutions from which the K 's were calculated contained iodine at $1.0 \times 10^{-4} M$ and thioacetamide varied from $1.0 \times 10^{-4} M$ to $3.3 \times 10^{-4} M$ for 17° and iodine at $0.75 \times 10^{-4} M$ and thioacetamide from $0.75 \times 10^{-4} M$ to $3.0 \times 10^{-4} M$ for 2.5°. All these solutions showed the 470 $m\mu$ isobestic point, tending to confirm the interpretation of 1:1 complex formation.

A similar situation was found with thiourea. The visible absorption of some solutions in which iodine was kept constant at a concentration of about $0.5 \times 10^{-4} M$ and thiourea varied from about $0.6 \times 10^{-4} M$ to $3.6 \times 10^{-4} M$, in order to maintain

the same conditions under which the K was determined, showed an isobestic point at about 480 $m\mu$.

Effects of Varying Iodine-Donor Mole Ratios.—When the concentration of thiourea in the solutions discussed in the preceding paragraph was increased to $1.1 \times 10^{-3} M$, the absorbance began to come below the isobestic point while the absorbance in the 400 $m\mu$ region due to the complex (since neither thiourea or iodine absorb in this region at the concentrations employed here) also decreased. This indicates that the equilibrium of 1:1 complex formation is being disturbed in some way that involves a decrease in the amount of free iodine as well as a decrease in the concentration of the complex. It was found, in analogy with thiourea, that solutions containing iodine constant at about $2 \times 10^{-4} M$ and thioacetamide greater than $3 \times 10^{-3} M$ began to have absorbances below the isobestic point, and their absorbances at the 400 $m\mu$ region began to decrease below that of solutions containing thioacetamide less than $1 \times 10^{-3} M$.

On the other hand, when the iodine concentration was made greater than that of thiourea, or thioacetamide, the visible isobestic points were maintained. But when the data from these solutions were used to make plots of equation 2, parabolic curves were obtained instead of the expected straight lines. This clearly indicates that something in addition to 1:1 complex formation is taking place in these solutions. Since the visible isobestic points were not disturbed, the possibility of a 2:1 (two iodine molecules to one donor molecule) complex existing in equilibrium with a much stronger 1:1 complex seems to be ruled out.

These thioacetamide solutions, with the iodine concentrations greater than that of the donor, were left to stand for a day and then measured. It was found that while the absorbance of the complex decreased that of the free visible iodine band increased, while on the other hand some solutions containing thioacetamide at concentrations greater than $3 \times 10^{-3} M$ (thioacetamide concentration more than thirty times greater than that of iodine) showed a decrease in both the absorbance of the complex and that of the free iodine band. These results indicate that in the latter case a reaction took place in which iodine acted as a catalyst.

A possible explanation of this catalyzing effect of iodine could be that in these solutions where iodine is at a greater concentration than thioacetamide, there is a large probability of a free iodine molecule encountering a molecule of the complex. The iodine molecule could attack the unoccupied donor site of the thioacetamide molecule which is already involved in complex formation at the stronger donor site. This unoccupied donor site will be much less of a donor because of the complexing at the other site, which would tend to pull charge from this unoccupied site due to both the resonance and inductive effects. Consequently, it seems likely that when the iodine approaches this weakened unoccupied donor site, instead of forming a stable complex bond at this secondary donor site with some electron density withdrawn from the primary donor site, the thioacetamide component of the complex undergoes some kind of internal rearrangement which frees the iodine molecule at the primary donor site and results in a net iodine catalyzed rearrangement of the thioacetamide molecule. Since the iodine absorption in these solutions returned to that of the free visible iodine band and was exactly the same as if no change had occurred to the visible iodine band, it must be concluded that this thioacetamide reaction product does not complex with iodine which would indicate that the electrons responsible for the initial complex formation are now involved in the bonding of this reaction product.

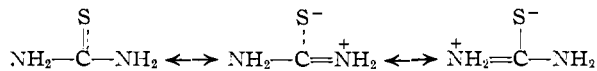
Discussion

Nature of the Bonding.—Both the K 's and the ΔH^0 's for the thiourea-iodine and thioacetamide-iodine complexes show that thiourea and thioacetamide are among the strongest donors toward iodine known.¹ The only stronger donors are tertiary amines while secondary amines¹² and alkyl selenides are of comparable ΔH^0 (Table III). Thiourea and thioacetamide are believed to be almost planar molecules in which the axes of the lone pair nitrogen

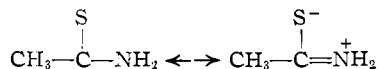
(11) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p. 160.

(12) H. Yada, J. Tanaka and S. Nagakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

orbitals are perpendicular to this plane and can overlap with the perpendicular p orbitals of the carbon and sulfur atoms, which form the thiocarbonyl double bond.¹³ Consequently, in valence bond terminology thiourea can be represented as having a three component resonance,¹⁴



and thioacetamide as having a two component resonance



This would tend to make the sulfur a stronger donor and the nitrogens less basic than if there were no resonance. There are three possible locations that might be considered as donor sites for thiourea and thioacetamide, namely: the nitrogen lone pair, the sulfur lone pairs, and the thiocarbonyl π electrons. [Sulfur has two different lone pairs, σ and π , in both sulfide and thiocarbonyl type bonding (Fig. 5).]

Regardless of whether the donor site is at sulfur or nitrogen, thiourea would still be expected to be a stronger donor than thioacetamide. This is because in thiourea two nitrogens are contributing electron density to the thiocarbonyl group and consequently each one should contribute less than the single nitrogen of thioacetamide. On the other hand, there are two dative structures contributing to the donor strength of sulfur in the case of thiourea compared to one for thioacetamide. Consequently, both the nitrogen and sulfur would be better donors in thiourea than in thioacetamide, in agreement with the present experimental results.

Because of the infrared evidence³ for amide-iodine coordination at oxygen and because lone pair electrons are better donors than bound π electrons one would expect a sulfur lone pair to be the donor toward iodine for both thiourea and thioacetamide. In the case of thioacetamide the n to π^* transition peak at $356 \mu\mu$ indicates that one of the sulfur lone pairs has a lower ionization potential than the thiocarbonyl π electrons, and this is another reason why one would expect a sulfur lone pair to be the donor.

Since the $p\pi_x$ and $p\pi_y$ lone pairs of sulfur (Fig. 5) are more directed and, consequently, should have a greater overlap ability than the σ_z lone pair, one would expect the former lone pair type orbitals to be the donors in complex formation with σ_u acceptors like the halogens. The geometry of the solid iodine-1,4-dithiane complex¹⁵ indicates that the donor orbital is nearly pure $p\pi_x$ whereas the geometry of the solid bromine-1,4-dioxane complex¹⁶ indicates that the donor orbital is a hybrid of $p\pi_x$ and σ_z . The geometry of halogen complexes with thiocarbonyl type donors is not known but that of the acetone-bromine complex¹⁷ indicates

(13) J. Stewart, *J. Chem. Phys.*, **26**, 248 (1957).

(14) The dative resonance contribution for thiourea has been estimated as between 20 to 30% for each of the dative structures, leaving 40 to 60% for the non-dative structures. W. K. Kumler and G. M. Fohlen, *J. Am. Chem. Soc.*, **64**, 1944 (1942).

(15) G. Y. Chao and J. D. McCullough, *Acta. Cryst.*, **13**, 727 (1960).

(16) (a) O. Hassel and J. Hvostlef, *Acta. Chem. Scand.*, **8**, 873 (1954). (b) O. Hassel, *Proc. Chem. Soc. (London)*, 250 (1957).

(17) O. Hassel and K. O. Stromme, *Acta Chem. Scand.*, **13**, 275 (1959).

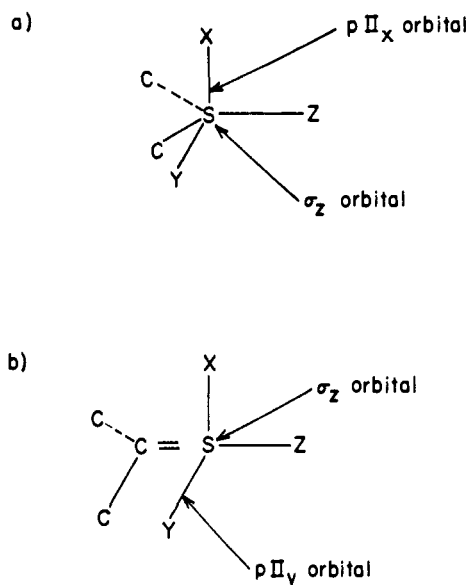


Fig. 5.—Geometry of the lone pair orbitals in sulfide (a) and thiocarbonyl (b) type bonding. (x axis is perpendicular to the y-z plane of the molecules).

that the donor orbital is a hybrid of $p\pi_y$ and σ_z similar to that of bromine-dioxane. Since the oxygen donor orbitals of both dioxane and acetone seem to be hybrids, whereas the sulfur donor orbital of dithiane seems to be nearly pure $p\pi_x$, one might expect the sulfur donor orbital in a thiocarbonyl-iodine complex to be nearly pure $p\pi_y$.

Thermodynamic evidence also indicates that a sulfur lone pair is probably the donor. The nitrogens in thiourea and thioacetamide are essentially primary with a decreased donor strength due to the resonance. Since primary amines have ΔH^0 's of about 7 kcal./mole,¹² if nitrogen were the donor site in these iodine complexes, one would expect the value of the ΔH^0 to be even smaller than 7 kcal./mole because of the resonance. The thiocarbonyl π electrons are already involved in bonding, and it is difficult to see how they could compete with a sulfur lone pair as the donor (a typical π donor such as benzene has a ΔH^0 of 1.3 kcal./mole for its 1:1 complex with iodine).¹⁸

The diethyl sulfide-iodine complex, in which the $p\pi_x$ sulfur lone pair is considered to be the donor, has a ΔH^0 of 7.8 kcal./mole.¹ Consequently, due to the resonance enhancement of the negative charge on the sulfur of the thiocarbonyl group and the consequent enhancement of the donor strength of the sulfur lone pair, one would expect the ΔH^0 for complexing with the sulfur lone pair to be somewhat greater than 7.8 kcal./mole, in accord with the experimental results for thiourea and thioacetamide. Acetamide has a ΔH^0 of 4.6 kcal./mole¹ and the difference between this value and the value for thioacetamide (dichloromethane being the solvent in both cases) is 3.6 kcal./mole. The difference in ΔH^0 between diethyl ether and diethyl sulfide (*n*-heptane being the solvent in both cases) is also 3.6 kcal./mole.¹ This difference in ΔH^0 for the ether and the sulfide should be mainly due to the dif-

(18) R. M. Keefer and I. J. Andrews, *J. Am. Chem. Soc.*, **77**, 2164 (1955).

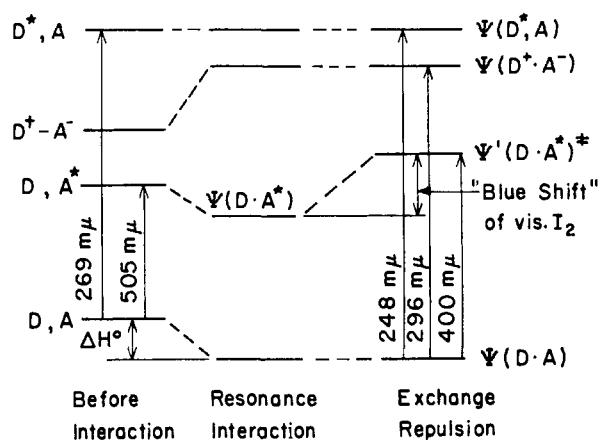


Fig. 6.—Schematic energy level diagram for the electronic spectral transitions of the thioacetamide-iodine complex. ‡Prime refers to exchange repulsion perturbation of $\psi(D \cdot A^*)$. $\psi(D \cdot A) \approx a\psi(D \cdot A) + b\psi(D^+ - A^-)$. $\psi(D^+ \cdot A^-) \approx b^*\psi(D, A) - a^*\psi(D^+ - A^-)$, where $a \approx a^*$ and $b \approx b^*$. $\psi(D \cdot A^*) \approx A\psi(D, A^*) + B\psi(D^+ - A^-)$.

ference in donor strength of the oxygen and sulfur lone pairs. This implies that the equivalent difference in ΔH^0 for acetamide and thioacetamide is also due to the difference in donor strength of the oxygen and sulfur lone pairs and consequently, that lone pairs are the donors in carbonyl and thiocarbonyl donor coordination with iodine.

Nature of the Spectra.—The work reported in this paper has shown the existence of three distinct electronic absorption bands for both the thiourea and thioacetamide 1:1 complexes with iodine. Two of these, the charge transfer and shifted visible iodine bands, are well known for molecular complexes of iodine. A third shifted band, characteristic of the donor in a complex, has not previously been directly observed for iodine complexes.¹⁹ This was mainly because either the solvent absorption, contact charge transfer absorption of iodine and the solvent, or the charge transfer band overlapped the long wave length donor bands; and, in addition, for weaker complexes the concentration of the donor was much greater than that of the complex so that any shifted donor absorption was obscured by that of the uncomplexed donor.

Table III shows that for most *n*-donor complexes the "blue shift" of the visible iodine band is considerably greater than the ground state ΔH^0 . On the other hand, the "blue shifted" thioacetamide band is shifted by an amount that is within experimental error of the ΔH^0 . Mulliken²⁰ has proposed a general explanation for the "blue shift" of the visible iodine band as being due to the increased exchange repulsion between the iodine molecule and the donor when the excited electron is introduced into the large σ_u orbital. The increase in extinction coefficient, on the other hand, has been attributed^{1,21} to a mixing of the upper level of the charge transfer band $\psi(D^+ - A^-)$ with the upper level of the visible

(19) However, for both the benzene-iodine and the benzene-bromine complexes an absorption band, distinct from the CT band, was indirectly detected around 260 $m\mu$. J. S. Ham, J. R. Platt and H. McConnell, *J. Chem. Phys.*, **19**, 1301 (1951).

(20) R. S. Mulliken, *Rec. trav. chim.*, **75**, 845 (1956).

(21) Private communication from Professor Mulliken.

TABLE III

A COMPARISON OF THE "BLUE SHIFT" OF THE VISIBLE IODINE BAND OF SOME *n*-DONOR-IODINE COMPLEXES WITH THE EXPERIMENTALLY DETERMINED ΔH^0

| Donor | $\Delta\lambda,^a m\mu$ | ΔE vis., kcal./mole | ΔH^0 exp., kcal./mole |
|--------------------------------|-------------------------|-----------------------------|-------------------------------|
| Methyl alcohol | 72 | 9.2 | 1.9 |
| Ethyl alcohol | 69 | 8.6 | 2.1 |
| Tri- <i>n</i> -butyl phosphate | 66 | 8.0 | 2.9 |
| N,N-Dimethylformamide | 61 | 7.7 | 4.0 |
| Diethyl ether | 60 | 7.2 | 4.2 |
| Diethyl ether | 44 | 5.2 | 4.3 |
| Acetamide | 62 | 8.0 | 4.6 |
| Diethyl disulfide | 62 | 7.4 | 4.6 |
| Ammonia | 92 | 11.7 | 4.8 |
| Ethylamine | 105 | 14.0 | 7.4 |
| Diethyl sulfide | 87 | 8.9 | 7.8 |
| Pyridine | 100 | 12.9 | 7.8 |
| Thioacetamide | ~100 | ~14.5 | 8.2 |
| Dimethyl selenide | 82 | 10.6 | 8.5 |
| Thiourea | ~100 | ~14.5 | 9.6 |
| Diethylamine | 112 | 15.2 | 9.7 |
| Triethylamine | 108 | 14.3 | 12.0 |
| Thioacetamide ^b | 21 | 9.0 | 8.2 |

^a See ref. 1 for source of data. ^b Thioacetamide 269 $m\mu$ band shift.

iodine band $\psi(D, A^*)$. Such mixing would have as a consequence that the weaker iodine band acquires intensity from the stronger CT band.

However, in the case of the shifted thioacetamide band, which is already intense, even if there were some mixing with the CT band one would not expect much change in intensity. The 269 $m\mu$ band of free thioacetamide has been attributed to a transition involving the nitrogen lone pair-thiocarbonyl π electron system.⁸ If a sulfur lone pair is the donor, complex formation with iodine will result in a substantial positive charge on the sulfur atom since the thioacetamide-iodine complex is a fairly strong complex and should have a substantial dative charge transfer contribution to the ground state (estimated as 25% for pyridine and 59% for triethylamine in their iodine complexes).¹ Such a positive charge on sulfur could produce a sufficient stabilization of the nitrogen lone pair-thiocarbonyl π electrons to explain the observed thioacetamide "blue shift". The preceding discussion is illustrated schematically, for the thioacetamide-iodine complex, by the energy level diagram of Fig. 6.

It is also interesting to note that the peaks of the charge transfer bands for both the thiourea and thioacetamide complexes are within a few $m\mu$ of those for diethyl sulfide and disulfide and, furthermore, that the intensity of CT bands of thiourea and thioacetamide are among the strongest known for iodine complexes, comparable to that of pyridine.¹

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