

ELECTRONIC ABSORPTION SPECTRA OF CHARGE TRANSFER INTERACTIONS INVOLVING SULFUR DONORS

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ABSTRACT

The charge transfer interactions of a series of differently substituted thioureas with iodine in dichloromethane have been studied by electronic absorption spectroscopy. The interaction of one thiourea, di-*i*-butyl thiourea with a strong acceptor, iodine monochloride has also been studied. The spectroscopic and thermodynamic data indicate that thioureas are strong electron donors. Phenyl isothiocyanate is, comparatively, a weaker electron donor.

THE charge transfer complexes formed by n donors with σ acceptors are highly stable^{1,2} whose enthalpies vary from 3 to 12 kcal mole⁻¹. Since sulfur atom has low ionization potential, it is expected that it will be a better n -electron donor than nitrogen atom. It will be interesting to investigate the lone pair donating ability of sulfur atom in comparison with that of nitrogen atom. For this purpose the compounds containing thio-carbonyl (C=S) group with varying substituents would be ideal. A few studies by Drago and coworkers³ and Rao and coworkers^{4,5} with I₂ as electron acceptor have shown that thiourea derivatives are stronger electron donors than amines. Another aspect of interest is that in thiourea derivatives, it is possible that the interaction may occur through nitrogen or sulfur atoms. In view of the exceptionally strong electron donating ability of substituted thioureas, it was considered interesting to examine the interaction of some more thioureas containing widely varying substituents with molecular iodine. Since iodine monochloride is considered to be a better electron acceptor than iodine, the study of the interaction of a few thioureas with iodine monochloride would be of value. The interaction of phenyl isothiocyanate with iodine has also been studied.

MATERIALS AND METHODS

The thioureas were prepared by the reaction between corresponding amines and isothiocyanate and purified⁶. All the solvents and other chemicals were purified by standard methods⁷. The electronic absorption spectra were recorded employing a Perkin Elmer Hitachi 139 Spectrophotometer equipped with a temperature regulated cell holder. Matched quartz cells (stoppered) of 1 cm path length were used. Equilibrium constants (K) were calculated from modified Benesi-Hildebrand equation⁸. The uncertainty in K is less than 10% and the uncertainty in $-\Delta H^\circ$ is ± 0.5 kcal mole⁻¹.

The approximate oscillator strengths (f) for the shifted bands and for pure acceptors were calculated from the relation

$$f = 4.319 \times 10^{-9} (\epsilon_m \cdot \Delta \nu_{1/2})$$

where ϵ_m is molecular extinction coefficient at the maxima of the shifted band and $\Delta \nu_{1/2}$ is the width in cm⁻¹ of the shifted band at half intensity. The transition dipole moments (D) were calculated from the relation

$$D = 0.0958 \left[\frac{\epsilon_m \cdot \Delta \nu_{1/2}}{m} \right]^{1/2}$$

where ϵ_m and $\Delta \nu_{1/2}$ are same as above. ν_m is the frequency of the shifted band maxima in cm⁻¹.

RESULTS AND DISCUSSION

It can be seen from Table I that N-phenyl, *i*-propyl N'-di-*i*-propyl thiourea (R₁ = C₆H₅, R₂ = R₃ = R₄ = *i*-C₃H₇, VII) has the highest equilibrium constant (18,500 l mole⁻¹) and $-\Delta H^\circ$ (14.5 kcal mole⁻¹) with iodine. In general, for the various thioureas, the equilibrium constants vary from 4,400 to 18,000 l mole⁻¹ and enthalpies ($-\Delta H^\circ$) vary from 9.6 to 14.5 kcal mole⁻¹. The magnitudes of these values suggest that the substituted thioureas under study are quite a strong electron donors towards the acceptor iodine. The ranges of values obtained for K and $-\Delta H^\circ$ are close to those obtained by Rao and coworkers⁴ on simple alkyl substituted thioureas. It can further be seen that in a series of phenyl thioureas, increasing alkyl group substitution, increases the equilibrium constants. Thus, simple phenyl thiourea (R₁ = C₆H₅, R₂ = R₃ = H, II) has an equilibrium constant of 5,600 l mole⁻¹. The introduction of the one methyl group as in the case of N-phenyl N'-methyl thiourea (R₁ = C₆H₅, R₂ = R₃ = H, R₄ = CH₃, III) increases the equilibrium constant to nearly twice the value (12,800). Introduction of three methyl groups as in N-phenyl, methyl N'-dimethyl thiourea (R₁ = C₆H₅, R₂ = R₃ = R₄ = CH₃, V) increases the equilibrium constant to 16,270 l mole⁻¹. Similar

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TABLE I
 Spectroscopic and thermodynamic data for Iodine- $R_1R_2NCSN'R_3R_4$ systems in dichloromethane

| No. | Name of Thiourea | Formula | | | | λ CT (nm) | ϵ | f |
|------|--------------------------------------------------------------|-------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|-------------------------|------------|-------------------------|
| | | R_1 | R_2 | R_3 | R_4 | | | |
| I | Thiourea ^(a) | H | H | H | H | 298 | 52,000 | 1.20 |
| II | Phenyl thiourea | C ₆ H ₅ | H | H | H | 302 | 1,800 | 1.90 × 10 ⁻² |
| III | N-phenyl, N'-methyl thiourea | C ₆ H ₅ | H | H | CH ₃ | 300 | 1,560 | 1.60 × 10 ⁻² |
| IV | N-phenyl, N'-diethyl thiourea | C ₆ H ₅ | H | C ₂ H ₅ | C ₂ H ₅ | 304 | 1,450 | 1.90 × 10 ⁻² |
| V | N-phenyl, methyl, N'-dimethyl thiourea | C ₆ H ₅ | CH ₃ | CH ₂ | CH ₂ | 310 | 1,740 | 2.18 × 10 ⁻² |
| VI | N-phenyl, ethyl, N'-diethyl thiourea | C ₆ H ₅ | C ₂ H ₅ | C ₂ H ₅ | C ₂ H ₅ | 312 | 1,680 | 1.83 × 10 ⁻² |
| VII | N-phenyl, <i>i</i> -propyl, N'-di- <i>i</i> -propyl thiourea | C ₆ H ₅ | <i>i</i> -C ₃ H ₇ | <i>i</i> -C ₃ H ₇ | <i>i</i> -C ₃ H ₇ | 306 | 1,800 | 2.05 × 10 ⁻² |
| VIII | N-phenyl, <i>n</i> -butyl, N'-di- <i>n</i> -butyl thiourea | C ₆ H ₅ | <i>n</i> -C ₄ H ₉ | <i>n</i> -C ₄ H ₉ | <i>n</i> -C ₄ H ₉ | 308 | 1,600 | 1.90 × 10 ⁻² |
| IX | N-phenyl, N'-bromo-pyridyl thiourea | C ₆ H ₅ | H | H | Br-pyridyl | 332 | 1,902 | 7.14 × 10 ⁻² |
| X | N- <i>p</i> -tolyl, N'-pyridyl thiourea | <i>p</i> -tolyl | H | H | Pyridyl | 320 | 3,050 | 8.50 × 10 ⁻² |
| XI | Phenyl isothiocyanate | .. | .. | .. | .. | 310 | .. | .. |

| No. | Name of Thiourea | D (Debye) | K (litre mole ⁻¹) (30°) | - ΔH° (kcal mole ⁻¹) | - ΔS° (e.u.) | b^2/a^2 |
|------|--------------------------------------------------------------|--------------|-------------------------------------------|--------------------------------------------------|------------------------------|-----------|
| I | Thiourea ^(a) | 8.75 | 4,400 | 9.6 | 14.7 | 0.10 |
| II | Phenyl thiourea | 1.60 | 5,600 | 11.2 | 19.8 | 0.12 |
| III | N-phenyl, N'-methyl thiourea | 1.55 | 12,800 | 14.3 | 28.4 | 0.15 |
| IV | N-phenyl, N'-diethyl thiourea | 1.23 | 14,300 | 13.0 | 23.9 | 0.14 |
| V | N-phenyl, methyl, N'-dimethyl thiourea | 1.15 | 16,270 | 13.2 | 24.3 | 0.15 |
| VI | N-phenyl, ethyl, N'-diethyl thiourea | 1.21 | 16,420 | 14.0 | 26.9 | 0.15 |
| VII | N-phenyl, <i>i</i> -propyl, N'-di- <i>i</i> -propyl thiourea | 0.92 | 18,500 | 14.5 | 28.3 | 0.16 |
| VIII | N-phenyl, <i>n</i> -butyl, N'-di- <i>n</i> -butyl thiourea | 0.93 | 17,650 | 14.0 | 26.8 | 0.15 |
| IX | N-phenyl, N'-bromo-pyridyl thiourea | 2.25 | 14,230 | 12.5 | 22.3 | 0.15 |
| X | N- <i>p</i> -tolyl, N'-pyridyl thiourea | 2.25 | 16,190 | 13.3 | 24.6 | 0.15 |
| XI | Phenyl isothiocyanate | .. | 53.0 | 3.6 | 4.0 | 0.04 |

thing happens with ethyl, *i*-propyl and *n*-butyl substituents. These variations are clearly due to the inductive effects of the alkyl substituents. The replacement of one of the hydrogens in phenyl thiourea by a bromoperidyl group ($R_1 = C_6H_5$, $R_2 = R_3 = H$, $R_4 = Br$ -Pyridyl, IX) enhances the equilibrium constant and $-\Delta H^\circ$. In the case of *N-p*-tolyl, *N'*-pyridyl thiourea ($R_1 = p$ -tolyl, $R_2 = R_3 = H$, $R_4 =$ pyridyl, X), where we have bulky substituents on either side, the equilibrium constant is 16,190 l mole⁻¹ and $-\Delta H^\circ$ is 13.3 kcal mole⁻¹. Steric effects do not seem to play a major role in these interactions.

In the infrared spectra of all the thioureas, the mixed vibration bands with appreciable contribution of the C=S stretching vibration (~ 1070 cm⁻¹) showed lowering of frequency and increases in intensity. This shows that the interaction of iodine occurs through the sulfur atom and not nitrogen.

The oscillator strength of CT bands are appreciable suggesting thereby stronger mode of interaction between iodine and alkyl thioureas. The b^2/a^2 values are a little higher than those for simple alkyl substituted thioureas.

Next, the interaction of iodine monochloride with a few alkyl substituted thioureas have been attempted in dichloromethane as solvent. Unfortunately, thiourea and di-*t*-butyl thiourea gave precipitates with iodine monochloride in dichloromethane solvent system. Di-*i*-propyl thiourea did not give any precipitate and hence this system was investigated in detail. Here the concentration of di-*i*-propyl thiourea was kept constant and the concentration of iodine monochloride varied. The charge transfer transition was located around 305 nm, whose intensity increases with the increase

in iodine monochloride concentration. The band around 260 nm characteristic of C=S group in the thiourea, decreased with an increase in the concentration of iodine monochloride. An isobestic point was clearly seen around 270 nm. The equilibrium constant and enthalpy were found to be 18,000 l mole⁻¹ and 13.2 kcal mole⁻¹ respectively. The values are higher than those with iodine. This can be explained as due to high electron affinity of iodine monochloride.

Next, the interaction of iodine with phenyl isothiocyanate containing $-N=C=S$ group was investigated in dichloromethane. A charge transfer transition was observed around 310 nm and the equilibrium constant and enthalpy are estimated to be 53.0 l mole⁻¹ and 3.6 kcal mole⁻¹ respectively. This shows that the isothiocyanate group is not effective in charge transfer interactions. This is possibly due to the mesomeric interaction of the nitrogen with the thiocarbonyl group.

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AWARD OF RESEARCH DEGREE

Tamil Nadu Agricultural University, Coimbatore, has awarded the Ph.D. degree in Agriculture to Shri G. V. Kothandaraman, and Shri M. R. Iruthaya Raj.

Karnatak University, Dharwar, has awarded the Ph.D. degree in Chemistry to Shri Veerappa

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