Charge-Transfer Complexes Between Iodine and Substituted Thioureas: Determination of Thermodynamic and Spectroscopic Properties

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15 iodine complexes with substituted thioureas were investigated in dichloromethane solution by UV-visible spectroscopy, and their equilibrium constants, reaction enthalpies and molar absorption coefficients were determined. The influence of the substituents on the properties of the charge-transfer complexes is examined. A critical discussion of previously published data is given, where comparable data are available.

1. Introduction

Although charge-transfer (CT) complexes usually are quite weak complexes, the equilibrium constants and reaction enthalpies of n-donor-σ-acceptor complexes may show rather high values. The strongest n-donors are amines, N-oxides, alkyl sulfides, and thiocarbonyl donors, especially thioureas [1]. Thioureas show high donor abilities because of the high polarizability of sulfur and the increased electron density on the sulfur atom caused by resonance within the N-C-S moiety.

In the present study, iodine complexes of differently substituted thioureas were investigated by UV-visible spectroscopy; the influence of the substituents on the thermodynamic and spectroscopic properties of the complexes is discussed.

2. Experimental

2.1 Materials

The following thiourea derivatives were used as donors in the CT complexes with iodine as acceptor:

unsubstituted thiourea (H_4), dimethylthiourea (me), diethylthiourea (et), di-n-propylthiourea (n-prop), di-iso-propylthiourea (i-prop), di-n-butylthiourea (n-bu), di-iso-butylthiourea (i-bu), di-sec-butylthiourea (s-bu), di-tert-butylthiourea (t-bu), di-n-hexylthiourea (n-hx), dicyclohexylthiourea (c-hx), tetramethylthiourea (Me_4), dibenzylthiourea (benz), diphenylthiourea (phen), diallylthiourea (allyl).

The 13 disubstituted thioureas are N,N′-substituted derivatives. All thioureas were commercially available and were recrystallized before use. Most of them were recrystallized from toluene; H_4 was recrystallized from acetonitrile, me from benzene, Me_4 and allyl from cyclohexane, and n-hx from petroleum ether. The thioureas were stored at $\sim 5\,°C$. The unsubstituted thiourea was dissolved in dichloromethane by ultrasonic treatment at $40\,°C$ for 5 h.

Iodine (Aldrich, 99.999%) was sublimed and then stored over P_2O_5 in a desiccator. The iodine samples were handled under an argon atmosphere. Dichloromethane (Aldrich, spectroscopic grade) was dried over basic alumina and then rectified under argon. It was taken from the reservoir by application of a helium overpressure.

2.2 Instrumental

A UV-visible spectrophotometer (PERKIN ELMER, type LAMBDA 15, with fixed 1 nm option) was employed for the spectroscopic measurements. All spectra were taken with a 0.5 s time constant against the pure solvent. 22 mm $\varnothing$ quartz cells of 10 mm optical path were used in a laboratory made thermostatted cell holder. Temperature control was with a LAUDA water bath thermostat (LAUDA Germany, type K2R).

2.3 Procedure

All donor and acceptor solutions were freshly prepared on the day of use and were poured together immediately before the measurement. For one mea-

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suring series 6 donor solutions with variable concentrations and an iodine solution with a constant concentration were employed.

The absorption was read at the wavelength of the maximum of the CT band and additionally at 10 and 20 nm longer wavelengths. All measurement series were performed at 12, 20 and 28 °C. Control measurements at the end of a series showed that the absorption was stable over several hours.

The acceptor absorption is zero within the range of the charge-transfer band. Whenever there was a small donor absorption at the measuring wavelength, this was accounted for by subtracting the absorption of the respective pure donor solution. The residual error due to the difference of the absorption of the free donor in the complex solution and that of the pure donor solution was estimated to be non-significant in all cases.

2.4 Data Treatment

The Lambert-Beer's law

$$A = \varepsilon c_{AD} d \qquad (1)$$

is used, where A is the experimental absorbance reading, ε the molar (decadic) absorption coefficient (l/mol/cm) of the complex, c_{AD} the complex concentration (mol/l), and d the optical path (cm). Solving (1) with $d = 1$ cm for c_{AD} and putting c_{AD} into the definition equation of the complex equilibrium constant K,

$$K = c_{AD}/(c_A c_D), \qquad (2)$$

where c_A and c_D are the weighed-in concentrations of the acceptor and the donor, yields (after some simple recalculation) the following equation, often called Lang equation [2]:

$$c_A c_D/A = (c_A + c_D - A/\varepsilon)(1/\varepsilon) + 1/(K\varepsilon). \qquad (3)$$

This equation is applicable under the restriction that only one (1:1) complex is formed and neither the donor nor the acceptor show any absorbance in the wavelength region of interest. K and ε were determined using a computerized iterative linear regression procedure. It starts with an assumed reasonable value of ε in the term $(c_A + c_D - A/\varepsilon)$ and runs a linear regression analysis of $c_A c_D/A$ against $(c_A + c_D - A/\varepsilon)$, which yields a new value of ε from the slope. The procedure is repeated, now starting with the new ε. This iteration converged rapidly in all cases. As a test, also a multiple linear regression analysis was per-

formed according to

$$c_A c_D/A = 1/(K\varepsilon) + (c_A + c_D)(1/\varepsilon) - A(1/\varepsilon)^2, \qquad (4)$$

which directly derives from (3). The results were in good agreement with those from the iterative procedure. The latter was finally favoured since it was less sensitive to outliers than the multiple linear regression.

The enthalpy of complex formation was determined in the usual way from the temperature dependence of the complex equilibrium constant K using the relation

$$\Delta H = -R \frac{\partial \ln K}{\partial (1/T)}. \qquad (5)$$

3. Results

3.1 Spectra

The UV absorption spectra of the donor-acceptor solutions are quite similar for almost all investigated thiourea-iodine systems. As a representative example, the UV absorption spectrum of the di-n-hexyl-thiourea-iodine system is shown in Figure 1.

Figure 1 also includes the UV absorption spectrum of the highest concentrated pure donor solution, which shows that the donor absorption is very low at the wavelengths of interest around the absorption maximum of the complex.
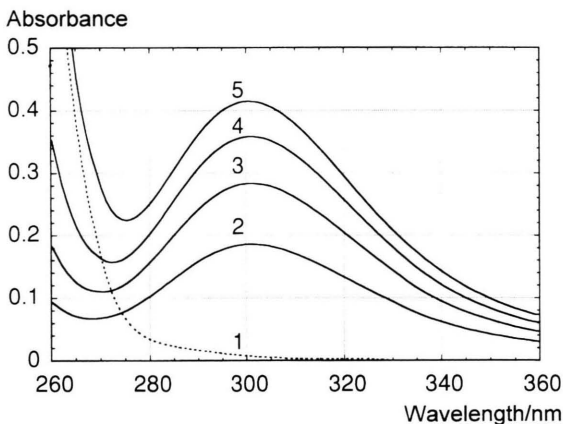
Fig. 1. Absorption spectra of the di-n-hexylthiourea-iodine system in dichloromethane:
1: donor $\qquad (c_D = 1.10 \cdot 10^{-4} \text{ mol/l}).$
2–5: donor-acceptor $(c_A = 1.05 \cdot 10^{-5} \text{ mol/l};$
$\qquad\qquad\qquad c_D = 1.10 \cdot 10^{-5} \text{ mol/l (2)},$
$\qquad\qquad\qquad c_D = 2.20 \cdot 10^{-5} \text{ mol/l (3)},$
$\qquad\qquad\qquad c_D = 4.40 \cdot 10^{-5} \text{ mol/l (4)},$
$\qquad\qquad\qquad c_D = 1.10 \cdot 10^{-4} \text{ mol/l (5)}).$

Absorbance
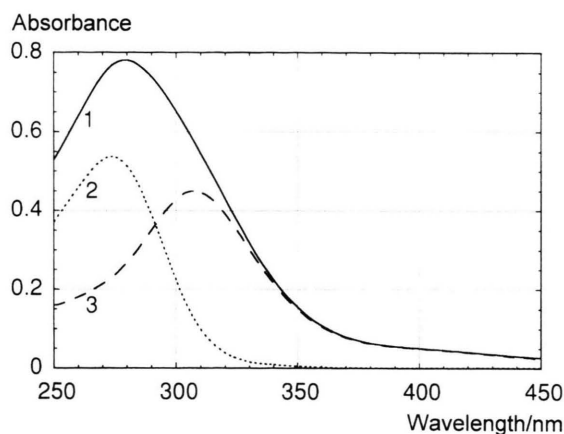

Fig. 2. Absorption spectra of the diphenylthiourea-iodine system in dichloromethane:
1: donor-acceptor ($c_D = 4.42 \cdot 10^{-5}$ mol/l, $c_A = 4.02 \cdot 10^{-5}$ mol/l);
2: donor ($c_D = 3.13 \cdot 10^{-5}$ mol/l);
3: curve 1 – curve 2 (spectrum of pure complex).

For the diphenylthiourea-iodine system the situation is more complicated, since the absorption maxima of the donor and the donor-acceptor solution almost coincide, as Fig. 2 shows. Nevertheless it was possible to separate the spectra and to obtain the complex spectrum. From the spectrum of the donor-acceptor mixture the donor spectrum was subtracted where the donor concentration corresponded to the calculated *free* donor concentration in the complex solution. The K value, being necessary for this calculation, was previously determined from the blue-shifted iodine band which is the second characteristic band of charge-transfer complexes with iodine [2].

3.2 Characteristic Data of the Complexes

Table 1 represents the spectroscopic and thermodynamic data for the 15 investigated thiourea-iodine complexes. All results are based on at least two series of measurements. The values of the molar absorption coefficient are average values of those resulting from the measuring series at the three different temperatures, and the values of the equilibrium constant are average values from the measurements at the three different wavelengths.

The last column of Table 1 cites the references to the CT complexes of the present communication. 7 complexes were investigated in our study for the first time. The thiourea-iodine and the tetramethylthiourea-

iodine complex were already studied in dichloromethane [2, 5]; the latter was also described in four additional solvents [3, 4, 6, 7]. All other 6 complexes were measured in chloroform [4, 8]. Statistical errors of K, ε and ΔH have not been included in Table 1, but were thoroughly studied. The following three types of statistical errors were calculated and are given as coefficient of variation (cv): the relative error as derived from the standard errors of the respective regression coefficients (cv < 7% for K, cv < 2% for ε and ΔH), the error between the measuring series (cv < 8% for K, cv < 4% for ε and ΔH) and the error of the mean of the three values at the three wavelengths or three temperatures, respectively (cv < 2% for K and ε).

Finally it should be noted that for some complexes the determination of K and ε was performed using the CT band *and* the blue-shifted iodine band within the same measuring series, for comparison. The concentrations were adjusted such that both (differently intense) bands revealed reasonable absorption values. As an example, for the unsubstituted thiourea-iodine complex $K_{CT} = 14\,700$ l/mol and $K_{vis} = 15\,400$ l/mol were obtained, which show perfect agreement within statistical limits. In this experiment, c_D was $3.5 \cdot 10^{-5} - 3.5 \cdot 19^{-4}$ mol/l and c_A was

Table 1. Spectroscopic and thermodynamic data for thiourea-iodine complexes.

Donor[a]	λ_{CT} (nm)	ε_{CT} (l/mol/cm)	$K_{20\,°C}$ (l/mol)	$-\Delta H$ (kJ/mol)	Ref.
H$_4$[b]	298	44 400	14 300	42.32	[2, 3]
me	298	43 400	75 700	47.05	[4]
et	300	44 000	80 400	46.96	[4]
n-prop	300	43 600	98 500	46.38	
i-prop	301	42 400	97 300	47.71	[4]
n-bu	300	43 600	102 100	45.45	
i-bu	301	43 300	107 200	45.96	
s-bu	301	43 000	125 900	46.32	
t-bu	304	44 300	245 600	46.77	[4]
n-hx	301	45 300	116 700	44.94	
c-hx	301	44 100	163 300	46.71	
Me$_4$	327	37 400	126 500	52.30	[3–7]
benz[c]	304	46 300	25 100	42.54	[8]
phen[c]	310[d]	37 100[d]	15 000[e]	42.64[e]	[4, 8]
allyl[f]	304				

[a] $c_D = 1.15 \cdot 10^{-5} - 1.15 \cdot 10^{-4}$ mol/l, $c_A = 1.05 \cdot 10^{-5}$ mol/l (in most measurements).
[b] $c_D = 3.2 \cdot 10^{-5} - 3.2 \cdot 10^{-4}$ mol/l, $c_A = 2.5 \cdot 10^{-5}$ mol/l.
[c] $c_D = 4.5 \cdot 10^{-5} - 4.5 \cdot 10^{-4}$ mol/l, $c_A = 4 \cdot 10^{-5}$ mol/l.
[d] Cf. explanations concerning Figure 2.
[e] Determined from the blue-shifted iodine band.
[f] Instable complex; cf. Section 4.4.

$4.5 \cdot 10^{-5}$ mol/l. For three substituted thiourea-iodine complexes both K_{CT} and K_{vis} were determined and also agreed very well.

4. Discussion

4.1 Effects of the Thiourea Substituents

4.1.1 Effect on λ_{CT} and ε_{CT}

Table 1 reveals that the iodine complexes of unsubstituted thiourea, of dibenzylthiourea, and of the 10 aliphatic dialkylthioureas possess very similar spectroscopic data ($\lambda_{CT} \approx 300$ nm, $\varepsilon_{CT} \approx 44\,000$ l/mol/cm). The tetramethylthiourea-iodine complex and the diphenylthiourea-iodine complex show higher λ_{CT} values and distinctly lower ε_{CT} values. In the former case, the donor molecule is not planar due to sterical hindrance of the four methyl groups [9], which reduces the NCS resonance, whereas in the latter case there is mesomerism between the NCS moiety and the aromatic substituents. Hence it must be concluded that the state of the NCS resonance within the donor determines the spectroscopic behaviour of the CT complex. It is interesting to note that thioureas with substituents showing + I or − I (inductive) effects (alkyl or benzyl moieties, respectively) yield iodine complexes of the same spectroscopic characteristics, thus indicating that the inductive effect does not play an important role.

4.1.2 Effect on K and ΔH

In contrast to the effect of the thiourea substituents on λ_{CT} and ε_{CT}, their effect on the K and ΔH values of the CT complexes is strongly determined by their inductive effect. This can be seen from Table 1 by following the series of di-n-alkylthiourea-iodine complexes (me, et, n-prop, n-bu, and n-hx), where K increases with increasing chain length. Going from me · I_2 to Me_4 · I_2, K gets larger due to the additional + I effect substituents. The correlation between the K values and the + I effect of the substituents can also be seen looking more closely to the series of dibutylthiourea-iodine complexes. Passing from n-bu · I_2 to i-bu · I_2, K does not change, in agreement with the fact that the carbon atom bound to the nitrogen is a primary in both cases. On the other hand, going from n-bu · I_2 via s-bu · I_2 to t-bu · I_2, which means going from a primary via a secondary to a tertiary carbon atom bound to the nitrogen, a strong increase of K occurs:

t-bu · I_2 has one of the highest K values so far observed for CT complexes. Passing from n-hx · I_2 to c-hx · I_2, which also means the step from a primary to a secondary carbon atom bound to the nitrogen, is accompanied by an increase of K. The K value of H_4 · I_2 is much lower than that of the aliphatic dialkylthiourea-iodine complexes, which is consistent with the above observations since there are no + I effect substituents. The low K value of benz · I_2 correlates with the − I effect of the benzyl groups, and the low K value of phen · I_2 with the − M effect of the phenyl groups.

The high ΔH values of the thiourea-iodine complexes indicate a strong interaction between the donor and the acceptor. The 10 aliphatic dialkylthiourea-iodine complexes possess rather similar ΔH values (45 to 47 kJ/mol). Me_4 · I_2 has the highest ΔH value (52.3 kJ/mol) within the whole investigated group of complexes due to the four + I effect substituents. H_4 · I_2, benz · I_2 and phen · I_2 have ΔH values of only ~ 42.5 kJ/mol corresponding to the missing + I, the − I and the − M effect substituents, respectively.

The steric effect can be seen in the following example: The K and ΔH values often show a parallel trend (e.g. for H_4 · I_2, benz · I_2 and phen · I_2 K and ΔH have a minimum), whereas Me_4 · I_2 possesses the maximum ΔH, but not the maximum K within the investigated complexes.

It is interesting to note that benz · I_2 and phen · I_2 show quite similar thermodynamic properties, although their substituents exhibit − I and − M effect respectively, thus indicating that the mesomerism itself does not affect the thermodynamic properties.

4.2 Comparison with Literature Data

In the present communication, all substituent thiourea-iodine complexes were measured in the same solvent (dichloromethane) in order to be able to attribute their spectroscopic and thermodynamic properties to the specific effects introduced by the different substituents (inductive, mesomeric and steric effects). Only for two complexes comparable literature data are available: the thiourea-iodine and the tetramethylthiourea-iodine complex were investigated in dichloromethane in detail by Lang [2, 5], and the former complex also in [3], where complex data very similar to those in [2] have been reported. A comparison between Lang's results and our own data is shown in Table 2.

Table 2. Comparison between literature data and the new results.

	Thiourea-iodine (in dichloromethane)		Tetramethyl-thiourea-iodine (in dichloromethane)	
	Ref. [2]	present study	Ref. [5]	present study
λ_{CT} (nm)	298	298	328	327
ε_{CT} (l/mol/cm)	52000	44400	36000	37400
$K_{20\,°C}$ (l/mol)	8500	14300	49000	126500
$-\Delta H$ (kJ/mol)	40.2	42.3	37.7	52.3

Strong differences between Lang's results and ours are found in the case of thiourea-iodine for ε_{CT} and K, and in the case of tetramethylthiourea-iodine for K and ΔH. These differences are discussed in the following.

4.2.1 The K Value of Tetramethylthiourea-iodine

$K_{20\,°C}$ is reported to be 49000 l/mol for the tetramethylthiourea-iodine complex [5], but was determined in the present communication to be 126500 l/mol. In discussing this discrepancy, a work of Caldin et al. [7] is very helpful: they report $K_{25\,°C} = 58000$ l/mol for this complex in 1-chlorobutane. Using their published value of ΔH, K can be recalculated for 20 °C to give $K_{20\,°C} = 83400$ l/mol in 1-chlorobutane. 1-chlorobutane is less polar than dichloromethane the relative permittivity of 1-chlorobutane is 7.4 [10], whereas that of dichloromethane is 9.1 [11]). For strong complexes, there is a parallel trend between the equilibrium constant and the solvent polarity. Hence, an even larger value than 83400 l/mol is to be expected in dichloromethane, in agreement with $K_{20\,°C} = 126500$ l/mol obtained in the present study.

4.2.2 The ΔH Value of Tetramethylthiourea-iodine

In [5] $\Delta H = -37.7$ kJ/mol is reported for the tetramethylthiourea-iodine complex, in contrast to the quite different value of $\Delta H = -52.3$ kJ/mol found in the present study. Again, the related result presented by Caldin et al. in [7] supports our result, since their ΔH value of 52.8 kJ/mol, determined in 1-chlorobutane, is in best agreement with our value in dichloro-

methane, as is to be expected since ΔH is usually not very dependent on the choice of the (inert) solvent.

4.2.3 The ε_{CT} Value of Thiourea-iodine

The ε_{CT} value of the thiourea-iodine complex reported to be 52000 l/mol/cm in [2] is considerably higher than what is found in the present study for all dialkylthiourea-iodine complexes (42400 to 45300 l/mol/cm) in dichloromethane, and is also larger than what is reported in [4] for chloroform solutions of this class of complexes (38000 to 40350 l/mol/cm). In addition, our own results show that the ε_{CT} values of all dialkylthiourea-iodine complexes are very similar to that of the thiourea-iodine complex itself (44400 l/mol/cm), which again raises some doubt as to the high ε_{CT} literature value.

4.2.4 The K Value of Thiourea-iodine

The $K_{20\,°C}$ value of the thiourea-iodine complex, reported here to be 14300 l/mol, is quite different from the literature value of 8500 l/mol [2]. Since there are no additional literature data available which could help to find the reason for this difference, some further experiments under modified experimental conditions were performed. The results of these experiments are presented in Table 3.

Table 3 shows that neither recrystallization of the donor nor fresh sublimation of iodine affect the resulting K value. In a glove box experiment all steps from preparing the solutions to their filling into quartz cells were carried out under an argon atmosphere to avoid access of moisture from the atmosphere. The results do not show any difference from those obtained by more simple procedures. Therefore, most probably differences in the solvent quality are responsible for the discrepancy between our results and the literature value of K.

Table 3. Equilibrium constants of the thiourea-iodine complex obtained under different experimental conditions.

Recrystallization of thiourea	Sublimation of iodine	Handling in	$K_{20\,°C}$ (l/mol)
−	−	air	14700, 14000, 13600
+	−	air	13900
−	+	air	14000
−	−	argon	14800, 15400

Consequently, two experiments have been performed to further study the role of the solvent quality [12]:

1. Determination of K of the thiourea-iodine complex in various dichloromethane qualities which differed concerning the purity, the water content, the presence of radicals etc. resulted in $K_{20 °C}$ values between 12 100 and 22 800 l/mol!

2. It could be shown that the donor is effectively degradated by radicals in the solvent, which results in a reduced observed K value. An estimation of this effect on the K value of the thiourea-iodine complex measured in rectified dichloromethane (cf. Section 2.1) shows that K, although being much larger than the literature value [2], is yet ∼ 12% too low. The ε_{CT} and ΔH values are only affected by 1 to 3%.

It would be possible to exclude radical effects by radical inhibitors, but since the latter can disturb the complex equilibrium (even at relatively low concentrations) in an unforeseeable way, no stabilizer was added to the solvent in the present study.

Hence, the small K value reported by Lang [2] for the thiourea-iodine complex must be considered as in error, the reason being a relatively high radical concentration in his solvent, although it was dried and distilled before use. No comment was made on whether these steps were performed under inert gas. Another possible reason for the differing K (and ε_{CT}) values may be seen in the *graphical* iterative evaluation of (3) in [2].

4.3 The Diallylthiourea-iodine Complex

The diallylthiourea-iodine complex is unstable under the experimental conditions. Nevertheless, an attempt was made to obtain some characteristic data of this complex, too, following its spectra only seconds after mixing the donor and acceptor solutions. 1.5 ml of the acceptor solution was added to 1.5 ml donor solution in the photometer cell which was then closed with a glass stopper, turned around once to achieve sufficient mixing and placed immediately in the cell holder. The photometer was directly started at 480 nm/min to take an absorption spectrum. Figure 3 shows an example of these time-dependent spectra: they were run 15 seconds after addition of the iodine solution and also after 2 and 5 minutes.

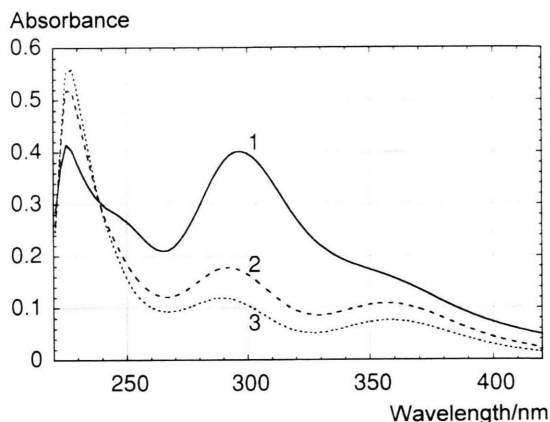The complex shows up by its 300 nm CT band immediately after mixing the solutions. The CT band

Fig. 3. Absorption spectra of the diallylthiourea-iodine system in dichloromethane:
1–3: donor-acceptor ($c_D = 4.08 \cdot 10^{-5}$ mol/l, $c_A = 4.10 \cdot 10^{-5}$ mol/l);
1: scan after 15 seconds; 2: scan after 2 minutes; 3: scan after 5 minutes.

vanishes within minutes, thus indicating some fast reaction of the CT complex. The thiocarbonyl band at 250 nm also decreases with time which means an opening of the C=S double bond during the reaction. A new band appears around 227 nm and increases with time which can be identified as an iodide band (in dioxane at 226 nm [13] originating from a decomposition product. The two bands at 291 and 357 nm are due to triiodide ions which are immediately formed by iodide in the presence of free iodine. The triiodide bands are reported to appear in 1,2-dichloroethane at 292 nm ($\varepsilon = 45 800$ l/mol/cm) and at 362 nm ($\varepsilon = 25 000$ l/mol/cm) [14].

Speculating on a possible reaction pathway, the following one is in agreement with the observed bands. After complex formation $I^{\delta+}$ is added to the C=C double bond of the allyl residue, and a cyclization to the five-membered ring compound 5-iodomethyl-2-allylamino-2-thiazoline occurs.

It is remarkable that the addition of iodine to diallylthiourea actually takes place, since iodine does not add to cyclohexene under comparable conditions. Moreover, the reactivity of the C=C double bond is lowered due to the neighbouring nitrogen atom. The addition of iodine to the allyl residue is made possible by polarization of the iodine in the preceding CT complex.

There are some hints from literature which support the postulated reaction mechanism. The reaction between an allylthiourea and bromine in an inert solvent like chloroform yields a 5-bromomethyl-2-amino-2-thiazoline [15] and is reported to be performed with cooling [16]. It is therefore justified to assume an analogous reaction between diallylthiourea and iodine in dichloromethane at room temperature.

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