A Calorimetric Study on Donor-Acceptor Complexes between Some Disulfides and Iodine

B. NELANDER

Thermochemistry Laboratory,* University of Lund, Lund, Sweden

Heats of formation and stability constants have been determined calorimetrically in ethylene chloride solution for complexes between iodine and methyl-, ethyl-, propyl-, isopropyl-, butyl-, tert-butyl-disulfide and 1,2-dithiane. Also, the stability constant for the iodine 1,2-dithiane complex was determined spectrophotometrically. The results are discussed in terms of donor ionization potentials and solvent solute interactions.

This investigation was undertaken for two reasons. In the first place it was felt desirable to exploit the calorimetric titration technique for simultaneous determination of stability constants and enthalpies of formation for weak donor acceptor complexes. This method was first systematically applied by Sillén and co-workers to studies of metal ion complexes in water solutions.

In the second place, in the course of a series of investigations on organic disulfides undertaken in this laboratory it was found desirable to study their donor properties in different environments. A systematic study of the enthalpies and entropies of formation of complexes between iodine and open and cyclic alifatic disulfides was therefore initiated, *i.a.* aiming at a possible correlation between donor properties and the dihedral angle between the CSS-planes.

EXPERIMENTAL

Materials

The alkyl disulfides were distilled in vacuum under nitrogen and, if necessary, further purified using preparative GLC (Wilkens Autoprep, apiezon). Purities as estimated from GLC (Pye Argon Chromatograph, 5 % apiezon): methyl, ethyl, isopropyl and tert-butyl disulfides no detectable impurities; propyl disulfide 99.1 % (impurity propyl isopropyl disulfide); butyl disulfide 98 %. A comparison between obtained density values and literature data is found in Table 1.

Table 1.

Disulfide	d_{25}	d_{20}	d_{25}(lit)	d_{20}(lit)
Me	1.0565	1.0621	1.0570[a]	1.0623[a]
i-Pr	0.9378	0.9425	0.9381[a]	0.9427[a]
Bu	0.9329	0.9372	0.9231[b]	0.9371[b]
			0.93245[c]	
t-Bu	0.9177	0.9220	0.9194[c]	0.9226[b]

[a] Ref. 1; [b] Ref. 2; [c] Ref. 3.

1,2-Dithiane was prepared from 1,4-dibromobutane over butane-dithiol-1,4 as described by Claesson *et al.*[4] The crude product was distilled at *ca.* 15 mm Hg, and the solid main fraction sublimed at 19 mm Hg. The product was stored in a refrigerator till it was used. Immediately before use it was sublimed at 1.5 mm Hg. Mp 31.0−31.6°C (32−33°C[4]). The melt was clear. A small sample of twice sublimed dithiane was dissolved in ether and analysed on a Pye Argon Chromatograph (5 % apiezon). No impurities could be detected.

Iodine, Merk (Pa), was used without further purification.

Ethylene chloride was treated as in Ref. 5.

Calorimetric procedures

For Me_2S_2, Et_2S_2, Pr_2S_2, $i-Pr_2S_2$, and Bu_2S_2 the calorimetric measurements were performed with an "isothermal jacket" titration calorimeter.[6] The calorimeter was charged with 62.68 ml of liquid; ethylene chloride or *ca.* 0.05 M I_2 in ethylene chloride. $[I_2]$ was determined titrimetrically. The disulfide was added in 0.75 ml portions (0.50 ml for Et_2S_2), 6 or 7 additions being made in each series (10 for Et_2S_2). Two or three series of additions were performed both for heat of solution and for heat of reaction measurements. In order to get a more even distribution of measured points the first additions in the second and third series were 0.50 ml and 0.25 ml, respectively. The heat equivalent of the calorimeter with its content was determined electrically by passing a known current for a given time (generally 3 min) through the heating element. The calibrations were performed on the system after each addition of disulfide. The initial and final thermistor resistances were obtained graphically in all cases.

For $t-Bu_2S_2$ the heat of solution experiments were performed as described above, but the heat of reaction experiments had to be done in a slightly different way because of a slow endothermic after reaction. After each addition of between 0.5 to 5 ml of disulfide, the calorimeter was emptied and recharged with iodine solution. Three series were made with slightly different iodine concentrations.

For 1,2-dithiane two different series of measurements were performed. In the first series the calorimetric measurements were performed with an "isothermal jacket" calorimeter,[7] charged with 101 ml liquid: ethylene chloride or 0.037 M I_2 in ethylene chloride. Immediately before each experiment the amount of dithiane to be used was sublimed at 0.1 mm Hg, pulverized in an agate mortar and filled into a glass ampoule (vol. 1 ml). The ampoule was closed with a silicon rubber stopper which was coated with a thin layer of silicon grease to prevent leakage. The sublimation before each ampoule filling took about 1 h and the time from the end of the sublimation till the ampoule was broken in the calorimeter was *ca.* 30 to 45 min. Nine heat of solution experiments and nine heat of reaction experiments were performed, in which the amount of dithiane in the ampoules varied from 60 to 500 mg.

In order to get larger variations in the amount of dithiane, a second series was done for which a calorimeter with a wider neck (inner diameter 20 mm instead of 15 mm) was built. This made possible the use of 2.5 ml ampoules. It proved necessary to reduce the gas volume over the calorimeter liquid in order to get a rapid equilibration after an ampoule was broken. Therefore, a thin-walled, hollow, closed glass cylinder with a central tube for the stirrer shaft was placed in the neck of the calorimeter after it had been charged. The modified calorimeter was tested by measuring the heat of solution of dithiane in ethylene chloride. The results did not differ significantly from those obtained in the first series. In this calorimeter 18 determinations of the heat of solution of dithiane in 0.02956 M I_2 in ethylene chloride (93 ml) were performed, the amount of dithiane in the ampoules varied between 66 and 709 mg. The calorimeter was calibrated electrically after each experiment.

Corrections for the heat of vaporization of solvent when an ampoule was broken and for the heat of breaking were determined in separate experiments for both calorimeters. The vaporization corrections measured agreed with what could be estimated from the heat of vaporization of ethylene chloride.

The spectrophotometric experiments were made using a Beckman DU spectrophotometer fitted with a thermostated cell compartment ($25.0 \pm 0.1°C$).

The optical density of six solutions, with $[I_2] = 0.276$ mM and [dithiane] from 11.1 to 67 mM, were measured at 4000 Å.

Calibrations

In the titration experiments the ε values ($\varepsilon = Q/\log R_i/R_f$; Q, electrical energy; R_i and R_f, initial and final resistances) varied linearly with the total amount of disulfides added, $\sum g_i$. No significant difference between solutions with and without iodine could be detected. $\varepsilon = \varepsilon_0 + k \times \sum g_i$.

In the dithiane experiments the ε values varied linearly both with the amount of substance in the ampoule, g, and with the weight of the empty ampoule, g_{glass}: $\varepsilon = \varepsilon_0 + kg + lg_{glass}$.

A summary of the results obtained is given in Table 2.

Table 2. Calibration experiments.

	ε_0	k	l	$\delta_{av}\%$
Me_2S_2	2423.6	31.08	—	0.30
Et_2S_2	2418.5	34.96	—	0.37
Pr_2S_2	2421.0	37.02	—	0.24
$i\text{-}Pr_2S_2$	2421.9	37.28	—	0.28
Bu_2S_2	2419.0	37.02	—	0.16
$t\text{-}Bu_2S_2$	2426.1	36.16	—	0.27
Dithiane$_1$	3537.2	29.6	5.6	0.08
Dithiane$_2$	3505.6	64.9	72.0	0.21

k and l were determined with the least squares method.
δ_{av}, average deviation

Heats of solution

In the titration experiments the measured values could, within the limits of error, be represented by quadratic functions of the form:

$$\sum_{i=1}^{n} Q_i = (A + B \sum_{i=1}^{n} g_i) \sum_{i=1}^{n} g_i \qquad (1)$$

or equivalent:

$$\frac{Q_n}{g_n} = A + 2B \left[\sum_{i=1}^{n-1} g_i + \tfrac{1}{2} g_n \right] \tag{2}$$

Q_i, the heat effect in the i-th experiment.

g_i, the amount of disulfide added in the i-th experiment.

The constants A and B were obtained from the measured values by least square analyses. Formula (2) was used since it makes it possible to exclude unsuccessful measurements (Table 3).

Table 3. Heat of solution experiments.

	A cal/g	B cal/g^2	Average error %
Me_2S_2	1.665	0.0274	0.29
Et_2S_2	3.502	0.0623	0.50
Pr_2S_2	4.818	0.0755	0.35
i-Pr_2S_2	4.921	0.0875	0.36
Bu_2S_2	5.793	0.0965	0.36
t-Bu_2S_2	5.067	0.0960	0.65

1,2-dithiane 37.25 ± 0.04 cal/g (standard dev. of the mean)

In the 1,2-dithiane experiments no variation of the heat of solution with the amount of disulfide dissolved could be detected.

Heats of reaction and stability constants

The heat effects (Q_i') from the heat of reaction experiments were corrected for heats of solution.

$$\sum_{i=1}^{n} Q_i = \sum_{i=1}^{n} Q_i' - \left(\sum_{i=1}^{n} Q_i \right)_{\text{soln}}$$

Heats of formation and stability constants for the complexes in ethylene chloride solutions were calculated under the assumptions that the sole reaction in the solutions was

$$R_2S_2(\text{soln}) + I_2(\text{soln}) \rightleftharpoons R_2S_2I_2(\text{soln}) \qquad \Delta H$$

and that the variation of the activity coefficients in the concentration interval used was insignificant.

$$\frac{[R_2S_2I_2]}{[R_2S_2][I_2]} = K$$

From this is derived:

$$\sum_{i=1}^{n} Q_i = \Delta H \, c \sum_{i=1}^{n} g_i \Big/ \left(a + b \sum_{i=1}^{n} g_i + \sqrt{(a + b \sum_{i=1}^{n} g_i)^2 - c \sum_{i=1}^{n} g_i} \right) \tag{1}$$

$a = (1/2)V(A + 1/K); b = (1/2)(1/M + 1/dK); c = AV/M$

K, stability constant, l/mole.

ΔH, heat of formation, cal/mole.

A, initial iodine concentration, mole/l.

V, initial volume, l.

M, molecular weight of the disulfide.

d, density of the disulfide, g/l.

The error sum

$$\sum_{i=1}^{n} \left| \sum_{j=1}^{i} Q_j - \left(\sum_{j=1}^{i} Q_j \right)_{\text{calc.}} \right| \qquad (n, \text{ total number of experiments}) \qquad (2)$$

was calculated by means of formula (1) for a network of ΔH and K values. The maximum allowable value of (2) was obtained from the assumption that the maximum error in $\sum Q_j$ was 1 % of the measured value. The $\sum Q_j$ values are of the order of 2 cal which can be determined within 0.5 % in a direct experiment, but they are obtained as differences between two quantities of the same order of magnitude. Thus they should be determined within 1 %. The maximum allowable value of (2) is thus given by the formula

$$\sum_{i=1}^{n} \frac{\left(\sum_{j=1}^{i} Q_j \right)^2}{100} \qquad (3)$$

The pairs of $K, \Delta H$ for which (2) had an absolute minimum were taken as the experimentally determined values, and the uncertainty limits were given by those $K, \Delta H$ pairs for which (2) was less than (3).

To test the method of calculation a series of $\sum_{j=1}^{i} Q_j$ values was constructed by means of (1), with typical values of the parameters. From this two further series were obtained. One was made by adding or subtracting randomly 0.1 to 0.5 % "errors" to the calculated $\sum_{j=1}^{i} Q_j$. The other was obtained by *adding* errors of the same order of magnitude to the calculated values. From these series, K and ΔH values were calculated in the manner described above.

Table 4. Test of calculation method.

Allowed error/exp.	series 1 exact			series 2 ± errors			series 3 + errors		
Error limits in	1 %	0.5 %	0.3 %	1.0 %	0.5 %	0.3 %	1 %	0.5 %	0.3 %
K	± 0.4	± 0.2	0.0	± 0.4	0.0	0.0	± 0.4	± 0.2	—
ΔH	± 0.2	± 0.1	0.0	± 0.2	0.0	0.0	± 0.4	± 0.1	—

In all cases the K and ΔH values used in the calculation minimized (2), $K = 4.0$, $\Delta H = 5.0$. The dependence of the error limits on the maximum value of (2) allowed is given in Table 4. In the third series no pair of $K,\Delta H$ made (2) less than the value given by 0.3 % errors of each point.

The results are given in Table 5. $\Delta G = -RT\ln K$. ΔS was calculated from ΔH and ΔG with the equation

$$\Delta G = \Delta H - T\Delta S$$

t is the thermostat temperature during the series.

Table 5. Results of calorimetric and equilibrium measurements.

	$t°C$	$-\Delta H$ kcal/mole	K l/mole	$-\Delta G$ kcal/mole	$-\Delta S$ e.u.
Me$_2$S$_2$	24.97	4.4 ± 0.1	2.4 ± 0.1	0.52 ± 0.03	13.1 ± 0.4
Et$_2$S$_2$	25.01	4.3 ± 0.1	3.1 ± 0.1	0.67 ± 0.02	12.1 ± 0.4
Pr$_2$S$_2$	24.98	4.5 ± 0.3	2.8 ± 0.4	0.61 ± 0.09	13.1 ± 1.0
i-Pr$_2$S$_2$	24.98	4.4 ± 0.2	3.5 ± 0.3	0.74 ± 0.05	12.4 ± 0.7
Bu$_2$S$_2$	24.98	4.3 ± 0.2	3.5 ± 0.4	0.74 ± 0.07	12.1 ± 0.7
t-Bu$_2$S$_2$	24.99	5.7 ± 0.2	6.8 ± 0.4	1.14 ± 0.04	15.4 ± 1.0
dithiane					
(1)	24.97	5.1 ± 0.4	10.3 ± 1.5		
(2)	24.97	4.6 ± 0.4	11.5 ± 1.9		
(1)$_s$	24.97	4.75 ± 0.10	11.6 ± 0.5		
(2)$_s$	24.97	4.60 ± 0.15	11.6 ± 0.5		
(1+2)$_{s,av}$	24.97	4.65 ± 0.15	11.6 ± 0.5	1.45 ± 0.02	10.9 ± 0.4

The values for t-Bu$_2$S$_2$ are average values of three series with 4, 3, and 8 experiments, respectively.

Dithiane (1)$_s$ and (2)$_s$ were calculated from the calorimetric data and the spectrophotometrically determined K value. (1+2)$_{s,\,av}$ is the weighted average of (1)$_s$ and (2)$_s$.

Since the calibration experiments were performed after the additions of disulfide were made, the K and ΔH values given refer to the initial temperature of the calorimeter, *i.e.* the thermostat temperature.

Spectrophotometry

The optical densities obtained were corrected for iodine and dithiane absorption. K and ε were determined from a modified Benesi-Hildebrand equation with the least squares method.[8] The following results were obtained

$$K = 11.6 \text{ l/mole} \qquad \varepsilon_{4000 \text{ Å}} = 5186$$

The K value agrees well with the calorimetric result.

In connection with these measurements spectra were taken for three solutions, one with $[I_2] = 1.87$ mM in ethylene chloride, a second with [dithiane]

$= 1.80$ mM, and a third with total concentrations of iodine and dithiane equal to those in the first and second solutions, respectively.

From the spectra the absorption maximum of the complex was found at 3510 Å, $\varepsilon_{max} = 14\ 500$.

Ionization potentials

The only disulfides for which ionizations potentials are given in the literature are Me_2S_2 [9-12] and Et_2S_2.[9,10,13] To make possible a correlation between the ionization potentials of disulfides and ΔH of formation for the charge transfer complexes between disulfides and iodine, ionization potentials were calculated with the method of Franklin [14] for the higher non-cyclic dialkyldisulfides, the parameters being taken from Refs. 13 and 14.

For dithiane (dihedral angle between the CSS/SSC planes $60° \pm 2$ [15]) and t-Bu_2S_2 (dihedral angle $ca.$ 100° as estimated from dipole moment [3]) the effect of the dihedral angle between CSS/SSC planes on the ionization potential had to be estimated. This was done under the assumption that $I_p = -\varepsilon$ where $-\varepsilon$ is the orbital energy of the highest occupied orbital. Expressions for the shift in orbital energy as a function of dihedral angle were taken from Ref. 16. The parameter γ of Ref. 16 was determined from the red-shift of 1,2-dithiolane (dihedral angle 27° [17]). These calculations gave the results given in Table 6. From the UV absorption maximum of the charge transfer complexes

Table 6. Ionization potentials.

	Measured eV	Obtained from CT spectrum eV	Calculated eV
Me_2S_2	8.46[a]		
	9.05[b]		
	8.53[c]		
	9.1[d]		
Et_2S_2	8.27[a]		8.32[e]
	8.85[b]		
	8.30[d]		
Pr_2S_2	—		8.31[e]
i-Pr_2S_2	—		8.18[e]
Bu_2S_2	—		8.30[e]
t-Bu_2S_2	—		8.02[e]
			7.81[f]
1,2-dithiane	—	7.62[g]	7.66[h]

[a]. Ref. 9.

[b]. Ref. 10.

[c]. Ref. 11.

[d]. Ref. 12.

[e]. Calculated with Franklin's method.

[f]. Calculated with simple molecular orbital theory as described above. The ionization potential for 90° dihedral angle was taken as 8.02 eV, the value obtained with Franklin's method.

[g]. Estimated as described below.

[h]. Calculated with simple molecular orbital theory as described above. The ionization potential for 90° dihedral angle was taken as 8.30 eV, the value for n-alkyl groups with more than two carbon atoms.

between a donor and iodine the ionization potentials of the donor can be estimated.[8] The UV absorption maximum of the complex between Et_2S_2 and iodine is 3030 Å.[18] From this value and Ref. 8 the ionization potential is calculated to be 8.89 eV, as compared with the photoionization value 8.27 eV. From the absorption maximum of the dithiane-iodine complex, determined in this work, 3510 Å, the ionization potential is calculated to be 8.24 eV. The difference between the ionization potentials should be given approx. by these calculations, if the parameters in formula (VI, 3) of Ref. 8 are of the same order of magnitude for disulfide-iodine complexes as for other iodine complexes. If we assumed this and assume that the photoionization value is correct we obtain the ionization potential of dithiane given in Table 6.

DISCUSSION

From Mulliken's theory of charge-transfer complexes [8] one would expect that the heats of formation of complexes between an acceptor and a homologous series of not too strong n-donors will become more exothermic in a regular way with decreasing ionization potential of the donor.

The result of this work shows that this is not the case for the complexes between iodine and a series of alkyldisulfides in ethylene chloride solution. One might think that the irregularities are due to differences in electrostatic interaction between iodine and disulfide in the complex. A disulfide with a larger dipole moment will have a larger dipole-induced dipole interaction with iodine in the complex. This cannot be the sole cause, however, for then dithiane complex should have a much more exothermic heat of formation than all other complexes studied.

	μ D
Me_2S_2	1.96 [20]
Et_2S_2	1.99 [20]
$n\text{-}Pr_2S_2$	1.96 [20]
	1.98 [19]
$n\text{-}Bu_2S_2$	1.99 [19]
	2.06 [3]
$t\text{-}Bu_2S_2$	1.86 [3]
1,2-Dithiane	2.5 [a]

[a] Estimated from bond-dipoles as in Ref. 3.

There are two effects that should decrease the heat of formation of the dithiane complex relative to those of the normal disulfides; the dipole moment of dithiane is higher and the ionization potential considerably lower.

Another reason for irregularities could be variations in van der Waals' interaction between iodine and different disulfides in the complex, but it is then hard to see why there is no difference between the heats of formation of $n\text{-}Pr_2S_2 \cdot I_2$ and $i\text{-}Pr_2S_2 \cdot I_2$.

To get an explanation for the irregularities in the variation of heat of formation with ionization potential we have to consider the differences in solvent-solute interactions between the free and complexed disulfides and the ethylene chloride. Ethylene chloride may exist in three conformations. In the most stable the chlorine atoms are in the *trans* position relative to the C—C bond

and the molecule has no dipole moment. In the two less stable conformations the chlorine atoms are in the *gauche* position and the molecule has a dipole moment of 2.54 D.[21] In the gas phase the energy difference between the trans and the gauche ethylene chloride is 1.22 kcal/mole,[21] but in the liquid phase it is about 0 kcal/mole. This means that the disulfides, with dipole moments about 2 D will interact electrostatically with the solvent. The interaction will probably increase the *gauche-trans* ratio (N_g/N_t) in the vicinity of the disulfide bond compared with the bulk of the solvent. A similar phenomenon has been observed by Denison and Ramsey in a study of dissociation of salts in ethylene chloride.[22] The interaction energy between a free disulfide molecule and the solvent will vary with the dipole moment of the disulfide and with the possibilities for the solvent molecules to approach the disulfide bond.

That the electrostatic effects discussed are of the correct order of magnitude can be seen from a simple calculation. The interaction energy between two dipoles, with dipole moments 2.00 D and 2.54 D, respectively, at a distance of 4 Å, is -2.3 kcal/mole when the dipoles are pointing in the same direction along the line joining them. If we decrease the 2.00 D dipole (n-Bu) to 1.86 D (t-Bu) the interaction energy is increased to -2.1 kcal/mole. When the complex is formed the iodine molecule approaches the disulfide bond and will then replace a number of solvent molecules, and the electrostatic interaction between the disulfide and the solvent is reduced. Thus a strong interaction between free disulfide and solvent will make the heat of formation of the complex less exothermic. For t-Bu$_2$S$_2$ the reduction in interaction energy will probably be less and for dithiane larger than for the normal disulfides, because of the differences in dipole moments and in steric requirements. Thus the difference in heat of formation of t-Bu$_2$S$_2$·I$_2$ and, for example, n-Bu$_2$S$_2$·I$_2$ should be due both to the lower ionization potential of t-Bu$_2$S$_2$ and to the lower solvent interaction energy for t-Bu$_2$S$_2$. For 1,2-dithiane the ionization potential is even lower than for t-Bu$_2$S$_2$ but the difference in solvent interaction between free and complexed dithiane should be much larger than for the other disulfides considered because of the much larger dipole moment. Thus the effect of the lower ionization potential of dithiane as compared with the other disulfides is largely cancelled by the solvent effect.

There are two effects that may cause the differences in entropies of complex formation obtained in this work. One is the solvent effect discussed above. When the complex is formed, the *gauche-trans* ratio of ethylene chloride in the vicinity of the solute is probably reduced to a value nearer to the equilibrium in the bulk of the solvent. This effect should give a positive contribution to the entropy of complex formation which is larger the stronger the interaction is between free disulfide and solvent. The other effect comes from the change in "internal entropy" of the disulfide upon complex formation. When the disulfide acts as a donor the potential barrier for rotation *cis* around the S—S bond is decreased but the "*trans* rotation" is inhibited. The decrease in potential barrier should be larger the lower the ionization potential of the disulfide. The inhibition of the *trans* rotation is common to all non cyclic disulfides. Both the solvent effect and the "internal entropy effect" predict a more negative entropy of formation for t-Bu$_2$S$_2$·I$_2$ than for the other complexes studied here. The solvent solute interaction between the free disulfide

and the solvent is weaker than for the other disulfides studied. Besides, the *cis* rotation is impossible for t-Bu$_2$S$_2$ for steric reasons, which makes it impossible for the complexed disulfide to exploit the decrease in potential barrier for rotation around the S—S bond. Dithiane interacts more strongly with the solvent than the other disulfides studied and has besides a lower ionization potential. Thus, from both effects, one will predict a less negative entropy of formation for the dithiane complex compared with the other disulfides studied. These predictions are verified by the measurements as is seen from Table 5.

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