ACTA CHEMICA SCANDINAVICA 26 (1972) 809–814

A Calorimetric and Spectrophotometric Study on Donor Acceptor Complexes Between Some Disulfides and Iodine

B. NELANDER and I. NORÉN

Thermochemistry Laboratory, Chemical Center, University of Lund,
S-220 07 Lund 7, Sweden

Stability constants for the iodine complexes of methyl-, ethyl-, isopropyl-, *tert*-butyl-, methyl *tert*-butyl disulfide and 1,2 dithiane have been determined spectrophotometrically in carbon tetrachloride solution.

Enthalpies of formation of these complexes have been obtained by combining the stability constants with calorimetric data.

In addition the stability constants of the propyl- and ethyl *tert*-butyl disulfide iodine complexes in carbon tetrachloride solution have been determined.

The results are discussed in terms of changes in structure of the disulfides upon complex formation.

The donor properties of organic disulfides have been the subject of a number of investigations.[1–8] The present paper is a continuation of a previous calorimetric study,[6] in which the heats of formation and free energies of formation of complexes between a series of disulfides and iodine in ethylene chloride were determined. The resulting heats of formation were at variance with what might be expected from theoretical considerations. It was suggested in Ref. 6 that these deviations from the expected behaviour were due to a solvent effect. The measurements have therefore been repeated in another solvent. Carbon tetrachloride was used since it can hardly be suspected to cause the same type of solvent effect suggested for ethylene chloride.[6] Besides, the visible spectrum of iodine does not differ significantly between gas phase and carbon tetrachloride solution, which indicates that there is no significant charge transfer interaction between iodine and carbon tetrachloride.

EXPERIMENTAL

Materials. *Me_2S_2* (Eastman chemicals) and *t-Bu_2S_2* (Fluka) were distilled twice in vacuum. *Et_2S_2* was prepared from the corresponding mercaptan as described by Vogel.[9] *i-Pr_2S_2* was prepared analogous to Et_2S_2. *Et t-BuS_2* was prepared from Et_2S_2 and t-BuSH as described by McAllan *et al.*[10] *Me t-BuS_2* was prepared analogous to Et t-BuS_2.

The alkyl disulfides were distilled in vacuum and, if necessary, further purified using preparative GLC (Wilkens Autoprep, apiezon). Purities as estimated from GLC (Pye Argon Chromatograph, 5 % apiezon): Me_2-, Et_2-, i-Pr_2-, t-Bu_2-, and Me t-Bu disulfides, no detectable impurities; Et t-BuS_2 99.5 % (impurity Et_2S_2); i-Pr_2S_2 99.1 % (impurity Pr i-PrS_2). A comparison between obtained density values and literature data is given in Table 1.

Table 1.

	d_{25} g/ml	d_{20} g/ml	d_{25} g/ml (lit.)	d_{20} g/ml (lit.)
Me_2S_2	1.0566	1.0621	1.0570[a]	1.0623[a]
Et_2S_2	0.9878	0.9925	0.9882[a]	0.9933[a]
n-Pr_2S_2	–	–	0.9549[a]	0.9596[a] 0.9597[d]
i-Pr_2S_2	0.9378	0.9425	0.9381[a]	0.9427[a] 0.9435[d]
t-Bu_2S_2	0.9186	0.9240	0.9194[c]	0.9226[b]
Me t-BuS_2	0.9685	–	–	–
Et t BuS_2	0.9434	0.9476	0.9425[a]	0.9471[a]

[a] Ref. 10.
[b] Ref. 14.
[c] Ref. 15.
[d] Ref. 16.

1,2-Dithiane was prepared from butanedithiol-1,4 as described by Claesson *et al.*[11] The crude product was sublimed at *ca.* 15 mmHg and then stored in a refrigerator till it was used. Immediately before use it was sublimed at 0.5 mmHg. M.p. 31.0 – 31.5°C (32 – 33°C[11]). 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 were detected.

Iodine, Merck *p.a.* and *carbon tetrachloride* (Fischer Scientific Co.) were used without further purification.

Spectrophotometry. The spectrophotometric experiments were carried out using a Beckman DU spectrophotometer fitted with a thermostated cell compartment (25.0 ± 0.1)°C. The optical densities (of six solutions) were measured at *ca.* 3850 Å and at 4400 Å, and the measurements were corrected for iodine and disulfide absorption. By fitting these data to a modified Benesi-Hildebrand equation [12] using the least-squares method the equilibrium constant, K_x, was determined.

Calorimetric procedure. The calorimetric measurements were carried out in an isothermal-jacket glass calorimeter which has been described in detail elsewhere.[13] Electrical calibrations were performed on the system before the reaction had taken place. The initial temperature and the amount of electrical energy used in a calibration experiment were chosen as close as possible to the initial temperature and heat evolved in the corresponding experiment. No significant difference in calibration constants between solutions with and without iodine could be detected. The final temperature for all experiments was 25.0 ± 0.1°C. In calculating the calorimetric results an average value from the calibration experiments was used.

The calorimeter was charged with 102.31 ml of liquid; CCl_4 or 0.05 M I_2 in CCl_4 (0.037 M for 1,2-dithiane). The sealed glass ampoule contained between 15 and 81 mmol disulfide (9 to 28 mmol for 1,2-dithiane). The heats of solution of the disulfides in carbon tetrachloride were determined in separate experiments.

In order to calculate heats of formation from the experimental values a correction for the dissociation of the complex had to be applied. To obtain this correction, K_c

Table 2.

	K_x l/mol CCl$_4$ (4400 Å)	K_x l/mol CCl$_4$ (3850 Å)	K_c l/mol CCl$_4$ (3850 Å)	K_c l/mol ethylene chloride
Me_2S_2	32.3 ± 3.2	27.3 ± 1.4	2.65 ± 0.13	2.4 ± 0.1
Et_2S_2	40.8 ± 4.0	38.0 ± 1.9	3.71 ± 0.18	3.1 ± 0.1
n-Pr_2S_2	43.6 ± 4.4	38.0 ± 1.9	3.76 ± 0.19	2.8 ± 0.4
i-Pr_2S_2	49.2 ± 5.0	44.5 ± 2.2	4.36 ± 0.22	3.5 ± 0.3
t-Bu_2S_2		59.2 ± 3.0	5.93 ± 0.29	6.8 ± 0.4
Me *t*-BuS_2	47.0 ± 4.7	37.0 ± 1.8	3.62 ± 0.18	–
Et *t*-BuS_2	–	42.0 ± 2.1	4.12 ± 0.20	–
1,2-Dithiane	–	102.3 ± 5.1	9.93 ± 0.49	11.6 ± 0.5

Table 3.

	Heats of formation		Heats of solution	
	$-\Delta H_f$ kJ/mol CCl$_4$	$-\Delta H_f$ kJ/mol ethylene chloride	$-\Delta H$ kJ/mol CCl$_4$	$-\Delta H$ kJ/mol ethylene chloride
Me_2S_2	21.2 ± 1.0	18.4 ± 0.4	-0.159 ± 0.004	-0.656 ± 0.002
Et_2S_2	18.7 ± 0.9	18.0 ± 0.4	0.452 ± 0.006	-1.791 ± 0.009
n-Pr_2S_2	–	18.8 ± 1.3	–	-3.030 ± 0.011
i-Pr_2S_2	19.8 ± 1.0	18.4 ± 0.8	0.556 ± 0.007	-3.095 ± 0.011
t-Bu_2S_2	26.4 ± 1.3	23.8 ± 0.8	1.138 ± 0.008	-3.781 ± 0.025
Me *t*-BuS_2	20.9 ± 1.0	–	0.594 ± 0.010	–
1,2-Dithiane	24.0 ± 1.2	19.5 ± 0.6	-18.150 ± 0.067	-18.737 ± 0.019

Table 4.

	$-\Delta G_f$ kJ/mol CCl$_4$	$-\Delta G_f$ kJ/mol ethylene chloride	$-\Delta S_f$ J/mol deg. CCl$_4$	$-\Delta S_f$ J/mol deg. ethylene chloride
Me_2S_2	2.41 ± 0.12	2.18 ± 0.13	63.1 ± 3.7	54.8 ± 1.7
Et_2S_2	3.25 ± 0.16	2.80 ± 0.08	51.9 ± 3.6	50.6 ± 1.7
n-Pr_2S_2	3.28 ± 0.16	2.55 ± 0.38	–	54.8 ± 4.2
i-Pr_2S_2	3.65 ± 0.18	3.10 ± 0.21	54.3 ± 3.9	51.9 ± 2.9
t-Bu_2S_2	4.41 ± 0.22	4.77 ± 0.17	73.9 ± 5.1	64.4 ± 4.2
Me *t*-BuS_2	3.19 ± 0.16	–	59.4 ± 3.9	–
Et *t*-BuS_2	3.51 ± 0.17	–	–	–
1,2-Dithiane	5.69 ± 0.28	6.07 ± 0.84	61.4 ± 4.9	45.6 ± 1.7

valus were calculated from the corresponding K_x values determined at 3850 Å, using values of average molar volume. The K_x values determined at 4400 Å were considered to be less reliable because a large correction for free iodine had to be applied in their determination.

The results are given in Tables 3 and 4. ΔG_f was determined from the formula $\Delta G_f = -RT \ln K_c$, ΔS_f, was calculated from ΔH_f, and ΔG_f by the equation $\Delta G_f = \Delta H_f - T\Delta S_f$. The ΔH_f values given are average values of 5 or 6 determinations.

DISCUSSION

In Fig. 1 $[\Delta G_f - \Delta G_f(\mathrm{Me_2S_2 \cdot I_2})]$ is plotted against the ionisation potential of the disulfide (both solvents).

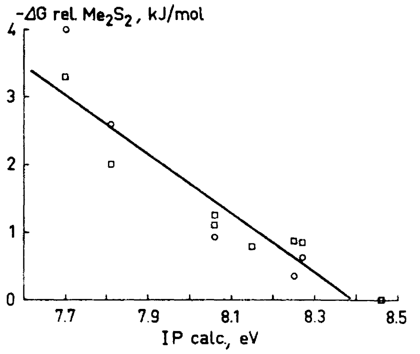

Fig. 1. Plot of $-(\Delta G_f - \Delta G_f(\mathrm{Me_2S_2 \cdot I_2}))$ *versus* ionisation potential of the disulfide as calculated in Ref. 7. ○, $|\Delta\Delta G_f|$ in ethylene chloride. □, $|\Delta\Delta G_f|$ in CCl_4.

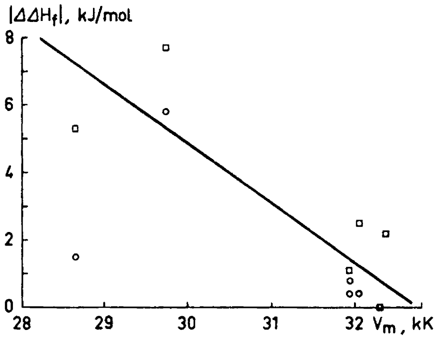

Fig. 2. Plot of $-(\Delta H_f - \Delta H_f(\mathrm{Me_2S_2 \cdot I_2}))$ *versus* the absorption maximum of the charge transfer band (see Ref. 7). ○, $|\Delta\Delta H_f|$ in ethylene chloride. □, $|\Delta\Delta H_f|$ in CCl_4.

Ionisation potentials were calculated in Ref. 7 using the theory of Franklin;[17] the influence of deviations of the dihedral angle, CSS/SSC, from 90° of the free disulfide were taken into account using simple MO-theory.[18]

From the figure is seen that ΔG_f in both solvents correlates reasonably well with the calculated ionisation potentials.

The ΔH_f values, given in Table 3, behave rather differently. The ΔH_f values of all disulfide iodine complexes studied here, with the exception of the complexes of 1,2-dithiane and t-$\mathrm{Bu_2S_2}$, are within 2 kJ/mol of -20 kJ/mol regardless of which solvent used.

They thus behave similarly to the positions of the maxima of their charge transfer absorption bands in UV.[7] In Ref. 7, simple MO-theory [18] and the relation between ionisation potential of the donor and the position of the charge transfer band given by Hastings *et al.*[12,19,20] were used to deduce that the disulfides probably undergo a change in dihedral angle upon complex formation and to estimate these changes for a series of disulfides. These ideas were further supported by a direct observation of the splitting between the $3p\pi$ and $3p\pi^*$ orbitals of the disulfide bond.[8] The splitting varied approximately as expected from the estimated changes in dihedral angle. The change in dihedral angle was found to be largest for $\mathrm{Me_2S_2}$, quite large for $\mathrm{Et_2S_2}$, but considerably smaller for noncyclic disulfides having secondary or tertiary carbon atoms next to the disulfide bond. If a change in dihedral angle is accompanied by a decrease in the enthalpy of formation of the complex, it may thus explain the unexpectedly large $|\Delta H_f|$ of the $\mathrm{Me_2S_2}$an d $\mathrm{Et_2S_2}$ complexes.

From the good correlation between the resulting ΔH_f, ΔS_f and ΔG_f values in both solvents it seems as if the importance of the disulfide-ethylene chloride

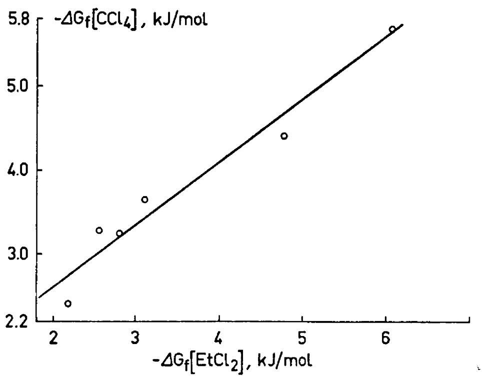

Fig. 3. $-\Delta G_f$, in CCl_4, *versus* $-\Delta G_f$, in ethylene chloride.

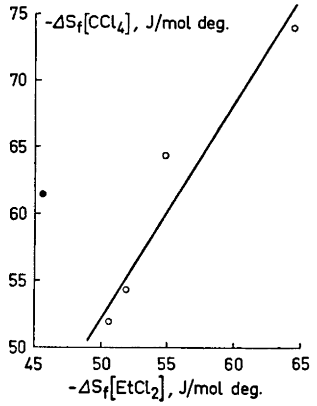

Fig. 4. $-\Delta S_f$, in CCl_4, *versus* $-\Delta S_f$, in ethylene chloride. ●, ΔS_f (1,2-dithiane).

interaction was overestimated in Ref. 6. It seems to be of importance only for 1,2 dithiane as indicated by the unexpectedly small $-\Delta H_f$ and $-\Delta S_f$ values of the dithiane-iodine complex in ethylene chloride compared to the other complexes studied.

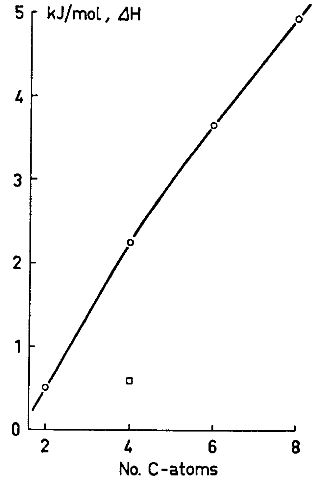

Fig. 5. ΔH for the process disulfide (soln., in CCl_4)→disulfide (soln., in ethylene chloride) *versus* the number of carbon atoms in the disulfide. □, of ΔH (1,2-dithiane).

Further support for the idea of a particularly strong interaction between ethylene chloride and dithiane is obtained from Fig. 5, which gives the heats of transfer from ethylene chloride to carbon tetrachloride as a function of the number of carbon atoms of the disulfide [disulfide (soln. CCl_4)→disulfide (soln. $EtCl_2$), ΔH].

It is seen from the figure that the heat of transfer is considerably more exothermic than might have been expected from the number of carbon atoms.

REFERENCES

1. Tsubomura, H. and Lang, R. P. *J. Am. Chem. Soc.* **83** (1961) 2085.
2. Good, M., Major, A., Nag-Chaudhuri, J. and McGlynn, S. P. *J. Am. Chem. Soc.* **83** (1961) 4329.
3. McGlynn, S. P., Nag-Chaudhuri, J. and Good, M. *J. Am. Chem. Soc.* **84** (1962) 9.
4. Moreau, W. M. and Weiss, K. *J. Am. Chem. Soc.* **88** (1966) 204.
5. Moreau, W. M. and Weiss, K. *Nature* **208** (1965) 1203.
6. Nelander, B. *Acta Chem. Scand.* **20** (1966) 2289.
7. Nelander, B. *Acta Chem. Scand.* **23** (1969) 2127.
8. Nelander, B. *Acta Chem. Scand.* **23** (1969) 2136.
9. Vogel, A. *A Textbook of Practical Organic Chemistry*, 3rd Ed., Longmans, London 1956.
10. McAllan, D.T., Cullum, T. V., Dean, R. A. and Fidler, F. A. *J. Am. Chem. Soc.* **73** (1951) 3627.
11. Claesson, G., Androes, G. and Calvin, M. *J. Am. Chem. Soc.* **83** (1961) 4357.
12. Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*, Springer-Verlag, Berlin—Göttingen—Heidelberg 1961.
13. Sunner, S. and Wadsö, I. *Science Tools* **13** (1966) 1.
14. Birch, S. F., Cullum, T. V. and Dean, R. A. *J. Inst. Petroleum* **39** (1953) 206.
15. Rogers, M. and Campbell, T. *J. Am. Chem. Soc.* **74** (1952) 4742.
16. Obolentsev, R. D., Netupskaya, S. V., Mashkina, A. V. and Gladkova, L. K. *Vostoch. Filialov. Akad. Nauk. SSSR* 1957, No. 10, 60; *Chem. Abstr.* **53** (1959) 273a.
17. Franklin, J. L. *J. Chem. Phys.* **22** (1954) 1304.
18. Bergson, G. *Arkiv Kemi* **12** (1958) 233.
19. Hastings, S. H., Franklin, J. L., Schiller, J. C. and Matsen, F. A. *J. Am. Chem. Soc.* **75** (1953) 2900.
20. Mulliken, R. S. and Person, W. B. *Ann. Rev. Phys. Chem.* **13** (1962) 107.

Received May 27, 1971.