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Equilibrium Studies on the Disproportionation Reaction Between Some Dialkyl Disulfides

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The disproportionation equilibrium between two symmetric disulfides and the corresponding mixed one has been determined at 25° and at 60° by use of vapor phase chromatographic technique. For diethyl disulfide in mixture with dimethyl- and di-*i*-propyl disulfide, respectively, the equilibrium constant is close to the statistically expected value, 4. For the pair diethyl- and di-*t*-butyl disulfide, the constant is 24. Within the uncertainty of the experiments, the equilibrium constant is temperature independent and thus ΔH is equal to zero. The strongly restricted internal rotation in di-*t*-butyl disulfide is responsible for the high value of the equilibrium constant.

It is a well-known fact that disulfides undergo disproportionation reactions according to

$$R_1SSR_1 + R_2SSR_2 \rightleftharpoons 2\ R_1SSR_2 \qquad (1)$$

This reaction has been used particularly for the synthesis of mixed disulfides [1-5].

McAllan *et al.*[5] have shown by distillation of equilibrium mixtures that the position of the equilibrium depends on the nature of R_1 and R_2. When R_1, R_2 were *n*-alkyl groups, the expected statistical distribution $(R_1S)_2{:}R_1R_2S_2{:}(R_2S)_2 = 1{:}2{:}1$ was reached, whereas for $R_1 = \mathrm{Et}$ and $R_2 = s\text{-Bu}$ and $t\text{-Bu}$, the ratios were found to be close to 1:4.5:1 and 1:6:1, respectively.

During the course of an extended investigation on the energetics of the disulfide bond it was found of importance to determine rather precisely the equilibrium constant for a number of dialkyl disulfides. Calvin *et al.*[6] studied a slightly different system, namely

$$\mathrm{BzSSBz} + \mathrm{HS(CH_2)_3SH} \rightleftharpoons 2\ \mathrm{BzSH} + \overline{\mathrm{S\text{-}(CH_2)_3\text{-}S}} \qquad (2)$$

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They were able to determine the equilibrium constant utilizing the fact that the disulfide 1,2-dithiolane has an absorption maximum at 330 mμ, whereas open chain dialkyl disulfides show a peak at 250 mμ. It is evident that this technique does not work in the case of a mixture of dialkyl disulfides.

The distillation method suffers from several disadvantages — it is slow and poorly quantitative, the separation efficiency is rather low, and, most important, it is difficult, if not impossible, to prevent completely the disulfide from further disproportionation during the distillation.

The vapor phase chromatographic technique was chosen as the analytical tool for the separation and quantitative determination of the homologous disulfides. This technique seemed to offer a number of advantages. The method is rapid and the separation is quantitative and of high efficiency. The duration of the sojourn of the unseparated mixture on the column is very short, decreasing the risk for any reaction to take place during the analysis. In a symmetric reaction like the one under investigation where absolute concentration values do not enter into the equilibrium equation, the relative concentrations can easily be determined from the evaluation of the areas under the peaks of the chromatogram and with an error of only a few per cent. By using an appropriate detector, the size of the sample can be kept very small, allowing the study of gas equilibria at low pressures without increasing the volume of the system inconveniently. Finally, the presence of impurities from side reactions will usually be immediately revealed during the analysis and is of no influence upon the desired result, provided the main reaction equilibrium has been attained.

Two conditions must be fulfilled in order to make the vapor phase chromatographic method useful. Reactions of any kind must not occur on the column, and a linear relationship must exist between the area under the peak on the chromatogram and the amount of substance passing the detector. Both conditions could be experimentally tested in our case and shown to be fulfilled.

CALCULATION

For reaction (1), the equilibrium constant K is given by

$$K = \frac{\mathrm{m}_{12}^2}{\mathrm{m}_{11} \cdot \mathrm{m}_{22}} = \frac{n_{12}^2}{n_{11} \cdot n_{22}} \qquad \text{(I)}$$

where m represents molarities and n the total number of moles present in a given sample; index 11 stands for diethyl disulfide, 22 for another symmetrical dialkyl disulfide, and 12 for the mixed disulfide.

The chromatograph is operated under such conditions as to fulfil the relation $n_i = k_i \cdot y_i$, where k_i is a constant and y_i the area under the peak on the chromatogram, related to the component i. In the present case, one of the reaction participants can be used as a reference substance, *e.g.*

$$n_{11} = k_{11} \times y_{11} \qquad \text{(IIa)}$$
$$n_{22} = k_{22} \times y_{22} \qquad \text{(IIb)}$$

which gives

$$\frac{n_{11}}{n_{22}} = k_{11,22} \times \frac{y_{11}}{y_{22}} \tag{III}$$

By calibrating the apparatus with known amounts of pairs of disulfides, the constants $k_{11,22}$, $k_{11,12}$ and $k_{12,22}$ can be separately determined and the relation

$$k_{11,22} = k_{11,12} \times k_{12,22} \tag{IV}$$

can be checked.

Finally, the equilibrium constant is

$$K = \frac{k_{12,22}}{k_{11,12}} \times \frac{y_{12}^2}{y_{11} \cdot y_{22}} \tag{V}$$

EXPERIMENTAL

Materials

Dimethyl disulfide and *diethyl disulfide* (Eastman chemicals) were distilled twice under reduced pressure to give pure fractions as judged from the chromatograms. *Di-i-propyl disulfide* and *di-t-butyl disulfide* were prepared from the corresponding mercaptans by oxidation with iodine, and distilled twice. After a final distillation at room temperature the purity was checked on the chromatograph.

Ethyl methyl disulfide was prepared both from dimethyl disulfide and ethyl mercaptan, as well as from a mixture of the symmetric disulfides with NaSEt as a catalyst. It was not feasible to obtain a completely pure sample by distillation (*cf.* Ref.[5]). The purest fraction contained 4 % of Me_2S_2 and no detectable amount of Et_2S_2. It was used in the experiments and proper correction was applied in the calibration runs.

Ethyl i-propyl disulfide and *t-butyl ethyl disulfide* were prepared according to method I and II, respectively, in Ref.[5]. They did not contain amounts of the symmetrical disulfides detectable on the chromatogram.

Methods

In the present investigation a Pye Argon chromatograph was used with a 5 mm column, 120 cm in length, filled with 100—120 mesh crushed brick stone, containing 5 % by weight of apiezon grease L. In the experiments with R_2 = Me the temperature was kept at *ca.* 105°C, when R_2 = *i*-Pr and *t*-Bu the temperature was *ca.* 115° and 125°C, respectively.

Calibration was carried out with all pairs of disulfides in molar ratios well covering the expected concentration ratios in the equilibrium mixtures. With the set-up given, in no case was the third disulfide formed which could be easily seen on the chromatogram. A possible disproportionation reaction occurring on the column was therefore judged to be completely insignificant *.

The equilibration experiments were carried out in a *cyclo*hexane solution (R_2 = Me, *i*-Pr) and the total concentration of disulfides was in most cases kept close to one mole per liter. The equilibrium was reached from both sides by use of an ionic catalyst (NaOH, method Ia), or by irradiation with light from a low pressure mercury lamp (method Ib). Experiments were carried out at 25° and 60°C. The solutions treated with sodium hydroxide were kept in 7 × 100 mm test tubes with ground glass stoppers. The catalyst was deposited from an ethanol solution as a very thin film on the inner surface of the

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* Note: With metal columns and high boiling esters as the stationary phase disproportionation occurred frequently on the column (*cf.* Ref. [7]).

tube before it was filled with the solution. The irradiated solutions were kept in quartz tubes with ground Pyrex glass stoppers.

Neither method Ia, nor method Ib worked very well. The equilibration time was often of considerable length and in many experiments the initial rate of reaction was extremely slow. The results from the experiments with R_2 = Me did indicate that a true equilibrium was not reached either from one or from both sides. For unknown reasons, all attempts to obtain an equilibrium mixture at 60°C with R_2 = *i*-Pr failed. Finally, when R_2 = *t*-Bu, neither method for equilibration was applicable. The reaction rate was extremely slow using the two-phase ionic system and the decomposition during irradiation was much faster than the disproportionation reaction. The equilibration runs were therefore carried out in the following solution (method II).

Freshly cut sodium (40 mg) was dissolved in 0.4 ml of ethanol, 96 % by volume, and 0.03 ml of *t*-BuSH was added together with 0.3 ml each of the symmetrical (or 0.6 ml of the mixed) disulfides. The solution was enclosed in a sealed Pyrex ampoule which was placed in a thermostat. In preparing the sample for the analysis, water was added to the content of the ampoule, the disulfide layer was washed once with water, and *iso*-pentane was added. The organic solution was washed twice with water, dried, and directly used for the analyses.

The same series of runs were performed with R_2 = Me, substituting EtSH for *t*-BuSH.

RESULTS

The results from the calibration experiments are found in Table 1. The concentration ratios between the two disulfides compared in each run were 1:2; 1:1 and 2:1 (R_2 = Me, *i*-Pr all combinations, and R_2 = *t*-Bu in mixtures between the symmetrical compounds). For both mixtures Et_2S_2-*t*-$BuEtS_2$ and *t*-Bu_2S_2-*t*-$BuEtS_2$, the ratios tested were 1:1; 1:2; 1:4 and 1:6. The same concentration ratio was measured in three parallel runs and each chromatogram was planimetered at least 6 times. The agreement between the calculated and the found $k_{11,22}$-values is satisfactory.

Table 2 gives a summary of the equilibrium measurements. Although the time for the experiments extended over several months, equilibrium was not reached with method I (R_2 = Me). The experiments according to method II indicate that the true equilibrium is close to the value obtained with method I starting with the unsymmetrical disulfide. Although a number of trials were performed with R_2 = *i*-Pr at 60°C no acceptable values of the equilibrium constant were obtained.

Method II gave much more reproducible results. For R_2 = *t*-Bu, altogether 12 equilibrium experiments were started. In three cases at 25°C, however, equilibrium was not attained within 6 months.

The K-values of the disproportionation reaction have been used to calculate the accompanying changes in free energy at 25°C, ΔF_{298}, and in enthalpy at the average temperature 42°, ΔH_{313} (Table 3). Assuming ΔH to be temperature independent within the small interval studied and thus zero at 25°, the corresponding changes in entropy have been calculated and are given in the table.

Table 1. Calibration experiments.

R_2	$k_{11,12}$	$k_{12,22}$	$k_{11,22}$	
			calc.	found
Me	1.04 ± 0.02	1.03 ± 0.02	1.07 ± 0.03	1.11 ± 0.02
i-Pr	1.20 ± 0.03	1.18 ± 0.04	1.42 ± 0.05	1.40 ± 0.04
t-Bu	1.11 ± 0.02	1.40 ± 0.04	1.55 ± 0.04	1.60 ± 0.06

Table 2. Equilibration experiments.

Reactants	Method	Temp. °C	K	Mean value
$Et_2S_2 + Me_2S_2$	I a	25	5.2 ± 0.2	
	I b	25	5.0	5.1 ± 0.2
	I a	60	5.1	5.1 ± 0.2
$EtMeS_2$	I a	25	5.4	
	I b	25	5.7	5.55 ± 0.2
	I a	60	5.6	5.6 ± 0.2
$Et_2S_2 + Me_2S_2$	II	25	5.61	5.6 ± 0.1
	II	60	5.56	5.6 ± 0.1
$EtMeS_2$	II	25	5.68	5.7 ± 0.1
	II	60	5.50	5.5 ± 0.1
$Et_2S_2 + i\text{-}Pr_2S_2$	I a	25	4.30	4.15 ± 0.15
	I b	25	4.05	
Et $i\text{-}PrS_2$	I a	25	4.05	4.05 ± 0.15
$Et_2S_2 + t\text{-}Bu_2S_2$	II	25	24.6	24.65 ± 0.1
		25	24.7	
	II	60	24.5	
		60	24.5	24.60 ± 0.1
		60	24.8	
$t\text{-}BuEtS_2$	II	25	24.4	24.4 ± 0.1
		60	24.5	
		60	24.3	24.5 ± 0.1
		60	24.6	

Table 3. Free energy and enthalpy changes for the reaction $R_1SSR_1 + R_2SSR_2 \rightarrow 2\ R_1SSR_2$

R_2	ΔF_{298}	ΔH_{315}	ΔS
Me	−1.020 ± 0.015	0.0 ± 0.15	3.42
i-Pr	−0.840 ± 0.015		2.82 *
t-Bu	−1.895 ± 0.015	0.0 ± 0.05	6.36

DISCUSSION

Provided the statistical distribution is the only factor governing the equilibrium between the two symmetric and the corresponding mixed disulfide, the equilibrium constant should be 4, ΔH should equal zero and ΔS should be R ln 4 = 2.76 e.u. The experimental results clearly lend support to the suggestion that this is principally true for $R_2 = i\text{-Pr}$ and also almost so for $R_2 =$ Me. When $R_2 = t\text{-Bu}$ the equilibrium constant is 6 times as large as is

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* ΔH assumed to be = 0. The statistical value of $K = 4$ gives $\Delta S = 2.76$ e.u.

required from statistical grounds. One explanation could be that the di-*t*-butyl disulfide is sterically strained while *t*-butyl ethyl disulfide is not or only to a small extent. However, this should be reflected in the ΔH-value which then must be negative with about 1 kcal·mole^{-1} for the forward reaction. The experimentally found value, $\Delta H \simeq 0$, rules out this possible explanation. The di-*t*-butyl disulfide molecule may be constructed from atomic models without introduction of strain from angle distortions and with a normal value (100°) of the dihedral angle between the C—S—S and S—S—C planes. In this model, however, the two *t*-butyl groups are very close together and any rotation round the C—S bonds seems to be highly hindered. The free independent rotations of the two *t*-butyl groups can be accomplished only when the dihedral angle exceeds *ca.* 135°. On the other hand, the intramolecular freedom in the *t*-butyl ethyl disulfide is much greater. Thus, the increased probability for the formation of the mixed disulfide in this case is caused by the "release" of conformations when the di-*t*-butyl disulfide molecule breaks up.

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