

EQUILIBRIUM STUDIES ON DISULPHIDES USING VAPOUR PHASE CHROMATOGRAPHY*

C. J. OLANDER and S. SUNNER

Thermochemistry Laboratory, University of Lund, Sweden

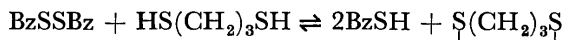
It is a well-known fact that disulphides undergo disproportionation reactions according to



This reaction has been used particularly for the synthesis of unsymmetrical disulphides¹⁻⁵ and McAllan *et al.*⁵ have shown that the position of the equilibrium depends on the nature of R' and R''. When R', R'' are n-alkyl groups the expected statistical distribution (R'S)₂: R'R''S₂: (R'S)₂ = 1:2:1 is reached, whereas for R' = Et and R'' = *sec*-Bu and *tert*-Bu the ratios were found to be close to 1 : 4, 5 : 1 and 1 : 6 : 1, respectively.

The disproportionation reaction occurs either in the presence of an ionic catalyst such as NaOH, Na₂S, or *tert*-BuSNa, or upon irradiation with ultra-violet light.

During the course of an investigation on the energetics of the disulphide bond it became important to determine the equilibrium constants for a number of dialkyl disulphides. Calvin *et al.*⁶ used the u.v.-spectrophotometric method to determine the equilibrium constant for a slightly different type of reaction, namely



This method could be used in this case as the 1,2-dithiolane ring has an absorption maximum at 330m μ , whereas open-chain dialkyl disulphides show a peak at *ca.* 250 m μ .

DISCUSSION OF METHOD

Vapour phase chromatography provides an obvious solution to the problem of finding an appropriate method for the separation and quantitative determination of the homologous dialkyl disulphides. This technique seems to offer a number of advantages for equilibrium studies, particularly on fairly simple systems.

(1) The separation efficiency can be made very high. The quantitative separation of *e.g.* Et₂S₂, *i*-PrEtS₂ and *i*-Pr₂S₂ can be achieved on a column only 120 cm in length.

(2) The presence of impurities formed in side reactions is instantaneously revealed in the chromatogram.

(3) The analysis is rapid, a run being completed within *ca.* 20 min. It is therefore frequently possible to determine the reaction rate by analysing samples from time to time.

*Published in *Acta Chem. Scand.*, **14**, 1509 (1960)

(4) The size of the sample can be very small—with a sensitive detector as little as 0.025 μl is sufficient. Thus, equilibrium conditions can be studied in a gas mixture at low pressures without increasing the volume of the system inconveniently.

Two conditions must be fulfilled to make the vapour phase chromatographic method useful.

(1) A linear relationship must exist between the amplified signal from the detector and the amount of substance passing the detector per unit time. Then the area under the peak of the chromatogram must be proportional to the total amount of substance. Within certain limits this can be achieved with different types of detectors, although some of them require carefully controlled operating conditions.

(2) Usually, the chromatographic column is operated at a temperature different from that at which the equilibrium is studied. It is therefore a necessary requirement that no reaction takes place on the column.

Both conditions can easily be tested with mixtures of known composition.

Calculation

To a good approximation, the equilibrium constant for the disproportionation reaction taking place in an inert hydrocarbon solution can be written

$$K = \frac{m_{12}^2}{m_{11} \times m_{22}}$$

where m_{11} and m_{22} are the molalities of the two symmetrical disulphides and m_{12} that of the unsymmetrical one. In a sample, the ratio between two molalities is identical with the ratio between the number of moles, n , of the corresponding components. The vapour phase chromatograph is operated under such conditions as to fulfil the relation $n_i = k_i \times y_i$, where k is a constant and y an area under a peak on the chromatogram, k and y being both related to the component i . In the present case one of the reaction participants can be used as a reference substance, thus

$$\frac{n_i}{n_j} = \frac{k_i}{k_j} \times \frac{y_i}{y_j} = k \times \frac{y_i}{y_j}$$

Hence

$$K = \frac{n_{12}}{n_{11}} \times \frac{n_{12}}{n_{22}} = k'k'' \frac{y_{12}}{y_{11}} \times \frac{y_{12}}{y_{22}}$$

The two constants k are evaluated from calibration experiments with known mixtures of disulphides and the areas y are measured with a planimeter or an electronic integrator.

EXPERIMENTAL

In the present investigation a Pye Argon chromatograph was used with a 5 mm column, 120 cm in length, filled with 100–120 mesh size crushed brick stone containing 5 per cent by weight of Apiezon grease L. For the pair of disulphides, Me_2S_2 and Et_2S_2 , the temperature was kept at 104°C.

EQUILIBRIUM STUDIES ON DISULPHIDES

Calibration was carried out with all three pairs of disulphides. Mixtures of dimethyl and diethyl disulphide in the molar ratios 2 : 1, 1 : 1 and 1 : 2 gave values of the corresponding constant, k''' ,

$$\frac{n_{11}}{n_{22}} = k''' \times \frac{y_{11}}{y_{22}}$$

equal to 0.89 ± 0.22 , 0.91 ± 0.03 and 0.88 ± 0.03 , respectively. The methyl ethyl disulphide was prepared by the disproportionation reaction and the mixture was carefully distilled. A fraction containing 96 per cent of MeEtS_2 and 4 per cent of Me_2S_2 (as determined by vapour phase chromatography) was used and appropriate corrections for the presence of Me_2S_2 were applied. The two constants were found to be: $k' = 1.03 \pm 0.02$ and $k'' = 0.96 \pm 0.22$. The ratio k''/k' , which by definition is equal to k''' , thus becomes 0.93 ± 0.03 , to be compared with the experimental (average) value 0.90 ± 0.02 . When Apiezon grease was used as the stationary phase no detectable disproportionation reaction occurred on the column.

All experiments were carried out in a cyclohexane solution and the total concentration of disulphides present was in most cases kept close to one mole per litre. The equilibrium was reached from both sides and the equilibration was brought about both by an ionic catalyst (NaOH) and by irradiation with light from a low pressure mercury lamp. Experiments were carried out at 25°C and at 60°C . The solutions treated with sodium hydroxide were kept in 7×100 mm test-tubes with ground glass stoppers. The catalyst was deposited as a very thin film on the inner surface of the tube before the solution was introduced. The irradiated solutions were kept in quartz tubes. Under the prevailing conditions equilibrium was established within 4 days in experiments with NaOH or within 4 hours of irradiation.

RESULTS

The results from the measurements on the pair dimethyl disulphide and diethyl disulphide are summarized in *Table 1*. The third column gives the side from which equilibrium has been reached. From the table it is evident that a true equilibrium has been reached and that the temperature dependence of the equilibrium constant is less than the uncertainty of the results.

Table 1

Temp. ($^\circ\text{C}$)	Treatment	Starting from	K
25	NaOH	symm.	5.2 ± 0.2
25	light	symm.	5.0 ± 0.2
25	NaOH	unsymm.	5.4 ± 0.1
25	light	unsymm.	5.7 ± 0.2
60	NaOH	symm.	5.1 ± 0.2
60	NaOH	unsymm.	5.6 ± 0.1

This investigation has been carried out under Contract AF 61 (052)-46 with Air Research and Development Command, United States Air Force, through its European Office.

References

- ¹ M. Kleiman, to Velsicol Corp., Chicago. *U.S. Pat.* 2,474,849. Appl. 20 Dec. 1946, Pat. 5 July 1949
- ² M. Kleiman, to Velsicol Corp., Chicago. *U.S. Pat.* 2,510,893. Appl. 20 Dec. 1946, Pat. 6 June 1950
- ³ W. A. Proell, to Standard Oil Co., Chicago. *U.S. Pat.* 2,521,870. Appl. 22 Oct. 1946, Pat. 12 Sept. 1950
- ⁴ W. A. Proell and C. E. Adams, to Standard Oil Co., Chicago. *U.S. Pat.* 2,557,312. Appl. 12 Febr. 1949, Pat. 19 June 1951
- ⁵ D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler. *J. Am. Chem. Soc.*, **73**, 3627 (1951)
- ⁶ J. A. Barltrop, P. M. Hayes and M. Calvin. *J. Am. Chem. Soc.*, **76**, 4348 (1954)