Cogwheel Effect in Dialkyl Disulfides

Bengt Nelander and Stig Sunner*

Contribution from the Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund, Sweden. *Received September 13, 1971*

Abstract: The disproportionation equilibrium $R'_2S_2 + R''_2S_2 \rightleftarrows 2R'R''S_2$ has been studied at 25° from both sides for a number of R′,R″ pairs of alkyl groups. In eight cases measurements were also carried out at 60°. Equilibrium constants were found to be close to the statistical value, $K = 4$, except in cases involving one tertiary α-carbon atom. The reaction was found to be thermoneutral or close to thermoneutral in all cases studied. A simple model is proposed which accounts for the variations in K in terms of coupled rotation between alkyl groups.

The disproportionation reaction $R'SSR' + R''SSR'' \rightleftarrows 2R'SSR''$ has been studied by a number of investigators.[1-4] The equilibrium constant was found to be close to $K = 4$ except in cases involving one tertiary α-carbon atom. Haraldson, *et al.*,[3] found $K = 24$ for R′ = Et, R″ = *tert*-Bu. The equilibrium was established from both sides and at 25 and 60°: $K_{25} = 24.6 \pm 0.2$ and $K_{60} = 24.5 \pm 0.3$. The enthalpy change for this reaction is thus close to zero. The authors suggested that, in di-*tert*-butyl disulfide, the two alkyl groups cannot rotate independently of each other. In the unsymmetrical disulfide formed in the reaction this restriction has to a large extent disappeared.

In order to elucidate the validity of this approach, a simple quantitative model of the rotation of the alkyl groups was developed. To test this model further experiments were carried out on altogether ten systems.

Experimental Section

Materials. Me_2S_2, Et_2S_2, Pr_2S_2, *i*-Pr_2S_2, Bu_2S_2, *i*-Bu_2S_2, and *tert*-Bu_2S_2 were commercial samples. *sec*-Bu_2S_2 and dicyclohexyl disulfide were prepared from the bromides as described by Vogel.[5] *tert*-AmSH was oxidized to the corresponding disulfide.[1] Neopentyl disulfide was prepared according to Bordwell, *et al.*[6] The unsymmetrical disulfides were all prepared by equilibration of a mixture of the corresponding symmetrical disulfides, followed by preparative glc.

All samples were found to be sufficiently pure as judged by analytical glc.

Methods. The only serious problem in this study (as in earlier work) was the extremely slow rate in attaining equilibrium when *tert*-alkyl groups were involved.[3,4] In fact, the present investigation was discontinued for a few years until it was found that iodine catalyzes the reaction.[7] Equilibrium could then be reached within a few days instead of months or even years.

Method III. *Ca.* 0.8 mmol of each disulfide was mixed with between 0.002 and 0.2 mmol of iodine in a glass ampoule, which was sealed and stored in a thermostat. Six ampoules were filled at a time, three from each direction. Also, two test tubes with fire-polished glass stoppers were charged and used to follow the reaction.

Samples of the reaction mixtures were diluted ten times with a suitable hydrocarbon (not interfering with the glc analyses; *n*-dodecane, *tert*-butylbenzene) and injected directly on the column (10% apiezone) on a Varian Aerograph Model 90-P gas chromatograph with a thermal conductivity type detector.

Comparison experiments between disulfide solutions with iodine and without (removed by thiosulfate treatment) gave the same results, indicating that the presence of iodine did not interfere with the analysis.

It is estimated that the formation of weak complexes between the disulfides and iodine led to an apparent equilibrium constant for the disproportionation reaction which is very significantly off. The discrepancy should be a function of the iodine concentration, and in principle it should be a simple matter to extrapolate to iodine concentration zero to obtain the true equilibrium constant. However, *tert*-alkyl disulfides react slowly and irreversibly with iodine, withdrawing iodine from complex formation with the disulfides making the extrapolation uncertain. A few equilibrium constants determined by use of methods I and II[3] were therefore determined also using iodine. The results were in reasonable agreement. For the Et-*i*-Pr system the apparent equilibrium constant was determined as a function of the iodine concentration. For iodine concentrations between 0.02 and 1 *M* no effect was observed, but for higher iodine concentrations (up to 6 *M*) the apparent equilibrium constant decreased rapidly with increasing iodine concentration. For the system Me-*tert*-Bu the equilibrium constant was much more sensitive to the iodine concentration, and it was therefore necessary to extrapolate the results to iodine concentration zero. The resulting equilibrium constant is 42.5 ± 3. For the remaining experiments method II of ref 3 was used. Calibrations were carried out as in ref 3.

Model

The starting point for an estimate of the equilibrium constant of a disproportionation reaction will be

$$K = Q(RR'S_2)^2/[Q(R_2S_2)Q(R'_2S_2)]e^{-\Delta E/(RT)} \tag{1}$$

$$Q(R_2S_2) = Q_{trans}{}^{R}Q_{rot}{}^{R}Q_{IR}{}^{R}(C_1S_1,C_2S_2)\prod_{i}^{3n-8}Q_i{}^{R}$$

$Q_{trans}{}^{R}$ and $Q_{rot}{}^{R}$ are the partition functions, respectively, for translation and rotation of the disulfide as a whole. $Q_{IR}{}^{R}(C_1S_1,C_2S_2)$ is the partition function for the two inernal rotations around the C–S bonds. It cannot be written as a product if the coupling between the two internal rotations is important. The Q_i values are partition functions for the remaining internal degrees of freedom.

To begin with, we assume $\Delta E = 0$. Secondly, we assume that all contributions from internal degrees of freedom cancel except for the internal rotations of the alkyl groups R and R′ around the C–S bonds. This approximation should be rather harmless except perhaps for the rotation around the S–S bond, and the CSS bending vibrations. Thirdly, we assume that the rotation and translation partition functions cancel except for the factors one-half from the rotational partition

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(2) S. F. Birch, T. V. Cullum, and R. A. Dean, *J. Inst. Petrol.*, 39, 206 (1953).

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(4) G. Dalman, J. McDermed, and G. Gorin, *J. Org. Chem.*, 29, 1480 (1964).

(5) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1959, p 497.

(6) F. G. Bordwell, B. M. Pitt, and M. Knell, *J. Amer. Chem. Soc.*, 73, 5004 (1951).

(7) B. Nelander, *Acta Chem. Scand.*, 25, 1510 (1971).

functions of the symmetrical disulfides. This approximation will at most change the estimated equilibrium constant by some 25%. We are now left with two internal rotations. In order to simplify matters we treat them classically

$$Q_{\mathrm{IR}}^{\mathrm{RR}'}(\mathrm{C_1S_1,C_2S_2}) = \int_0^{2\pi}\int_0^{2\pi}\int_{-\infty}^{+\infty}\int \exp\left(-\left(\frac{p_1^2}{2I_1} + \frac{p_2^2}{2I_2} + u^{\mathrm{RR}'}(\phi_1,\phi_2)\right)\Big/kT\right)\mathrm{d}p_1\mathrm{d}p_2\mathrm{d}\phi_1\mathrm{d}\phi_2$$

Here p_1 and p_2 are the angular momenta around the C–S bonds, I_1 and I_2 are the corresponding moments of inertia, ϕ_1 and ϕ_2 are the angular coordinates, and $u(\phi_1,\phi_2)$ is the potential energy as a function of these angles. The first two factors will cancel between numerator and denominator, and we are left with

$$K = 4\frac{\left(\int_0^{2\pi}\int_0^{2\pi} e^{-\frac{u^{\mathrm{RR}'}(\phi_1,\phi_2)}{kT}}\mathrm{d}\phi_1\mathrm{d}\phi_2\right)^2}{\left(\int_0^{2\pi}\int_0^{2\pi} e^{-\frac{u^{\mathrm{R}}(\phi_1,\phi_2)}{kT}}\mathrm{d}\phi_1\mathrm{d}\phi_2\right)\left(\int_0^{2\pi}\int_0^{2\pi} e^{-\frac{u^{\mathrm{R}'}(\phi_1,\phi_2)}{kT}}\mathrm{d}\phi_1\mathrm{d}\phi_2\right)}$$

From observations on stick and ball models it appears likely that the two rotating alkyl groups on each side of the disulfide bond will interfere, when carbon atoms in β position to the S–S bond on each side of the bond point toward each other. In order to account for this interaction in the simplest possible way we assume a potential function which is either zero or infinity. When the dihedral angles around the C–S bonds of two β carbon atoms are simultaneously in the interval $-(\pi/3 - \delta)$ to $\pi/3 - \delta$ (measured from the plane bisecting the angle CSS–SSC), the potential is infinite; elsewhere it is zero. In order to clarify what we mean, we will calculate $Q_{\mathrm{IR}}^{\mathrm{Et_2S_2}}(\mathrm{C_1S_1,C_2S_2})$ as an example. We measure ϕ_1 and ϕ_2 from the line joining the α carbon

$$\int_0^{2\pi}\int_0^{2\pi} e^{-\frac{u^{\mathrm{Et_2S_2}}}{kT}}\mathrm{d}\phi_1\mathrm{d}\phi_2 =$$

$$\left[\int_0^{\frac{\pi}{3}-\delta}\mathrm{d}\phi_1\left\{\int_0^{\frac{\pi}{3}-\delta}\mathrm{d}\phi_2 + \int_{\frac{\pi}{3}-\delta}^{\frac{5\pi}{3}+\delta}\mathrm{d}\phi_2 + \int_{\frac{5\pi}{3}+\delta}^{2\pi}\mathrm{d}\phi_2\right\} + \int_{\frac{\pi}{3}-\delta}^{\frac{5\pi}{3}+\delta}\mathrm{d}\phi_1\int_0^{2\pi}\mathrm{d}\phi_2 + \int_{\frac{5\pi}{3}+\delta}^{2\pi}\mathrm{d}\phi_1\left\{\int_0^{\frac{\pi}{3}-\delta}\mathrm{d}\phi_2 + \int_{\frac{\pi}{3}-\delta}^{\frac{5\pi}{3}+\delta}\mathrm{d}\phi_2 + \int_{\frac{5\pi}{3}+\delta}^{2\pi}\mathrm{d}\phi_2\right\}\right]e^{-\frac{u^{\mathrm{Et_2S_2}}}{kT}}$$

atoms. Taking into account that $u(\phi_1,\phi_2) = 0$ when at least one of the ϕ values is outside $(\pi/3 + \delta, \pi/3 - \delta)$ and $u(\phi_1,\phi_2)$ is infinite when both values are in this interval, we get

$$\int_0^{2\pi}\int_0^{2\pi} e^{-\frac{u^{\mathrm{Et_2S_2}}}{kT}}\mathrm{d}\phi_1\mathrm{d}\phi_2 = \frac{32\pi^2}{9} + \frac{8\pi}{3}\delta - 4\delta^2$$

The parameter δ is chosen to fit the experimental K value of the Et-*tert*-Bu system. The calculated equilibrium constants are given in Table I.

Table I

System	Equilibrium constant[a] Method III 25°	Method II 25°	Method II 60°	Model[e]
Me–Et		5.6[b]	5.6[b]	4.5
Me–*i*-Pr	6.0			6.9
Me–*tert*-Bu	42.5 ± 3[d]			49.0
Et–*n*-Pr	4.5	4.5	4.5	4.0
Et–*n*-Bu		4.3	4.5	4.0
Et–*i*-Bu		4.7	5.2	4.0
n-Pr–neo-Pe		4.8	4.8	4.0
Et–*i*-Pr	4.9	4.1[b]		4.8
n-Pr–*sec*-Bu		4.4[c]		4.8
Et–*sec*-Bu		5.1	5.9	4.8
n-Bu–C_6H_{12}		4.0	4.0	4.8
Et–*tert*-Bu	27	24.5[b]	24.6[b]	26.3
n-Bu–*tert*-Bu		21[c]		26.3
n-Pr–*tert*-Am			24.3	26.3
i-Pr–*tert*-Bu	15			12.5

[a] In all cases the reproducibility was within 5%. All equilibria were established from both directions and agreement was within 5%. [b] Reference 3. [c] Reference 4. [d] Extrapolated value, see text. [e] $\delta = \pi/72$.

Discussion

From the results given in Table I, it seems clear that in all cases, not including *tert*-alkyl groups, the interaction between the alkyl groups on both sides of the disulfide bond is small. Thus, the "driving force" of the disproportionation reaction is the lowering of symmetry going from reactants to products. The results of Haraldson, *et al.*,[3] show that the enthalpy of reaction is small also for the ethyl-*tert*-butyl system. We therefore have to ascertain why the entropy increase is much larger in cases involving *tert*-alkyl groups. To do this, Haraldson, *et al.*,[3] suggested that two *tert*-alkyl groups in the same disulfide cannot rotate independently of each other, but have to rotate together. The entropy increase should then be associated with the restoring of free rotation in the unsymmetrical disulfide. To put this suggestion on a quantitative basis the model described above was constructed. Considering the rather drastic approximations involved, the only real experimental test is the comparison between the calculated and experimentally determined ratio of the equilibrium constants of the methyl–, ethyl–, and isopropyl–*tert*-butyl systems.

We believe that the found agreement shows that the two alkyl groups on each side of the disulfide bond cannot rotate independently of each other. On the other hand it does not reveal the detailed nature of their interactions, although it is tempting to talk of a cogwheel effect. This effect must be rather common (*e.g.*, 2,2,4,4-tetramethylpentane, *tert*-$\mathrm{Bu_2C{=}O}$, and *o*-(*tert*-$\mathrm{Bu)_2C_6H_4}$), but as a rule it is inseparable from a more or less pronounced strain effect. The disulfide disproportionation reaction seems to represent a rather unique situation, where the strain effect is virtually absent.