A Note on the Depolymerization of Polymeric Disulfides

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In the course of an investigation of complexes of organic disulfides and iodine,[1-3] solid iodine was found to react with the solid polymers $(-S-(CH_2)_p-S)_n$ ($p = 3, 4, 5, 6, 10$) to form the corresponding cyclic monomers $(CH_2)_pS_2$.

This reaction is the reversal of the well-known polymerization of cyclic disulfides, which takes place spontaneously in the presence of a catalyst,[4,5] for instance iodine.[5] Thus, the free energy of the polymerization reaction is negative. It is expected to vary with ring size roughly as the free energy of polymerization of the cycloalkanes. For small p-values ($p < 5$) the deviations of the dihedral angle (CSS/SSC) from 90° in the monomers should be the dominating factor influencing the free energy of polymerization, while for the larger rings interaction in the alkane part of the ring ought to be more important. In the present case the solid polymers were mixed with *ca.* 2 mol of iodine per monomer unit. Therefore, differences in free energy of iodine-complex formation between monomer and polymer disulfide bonds have to be taken into account. The cyclic monomer $(CH_2)_4S_2$ is known to form a much stronger iodine complex than do ordinary noncyclic disulfides.[3] This is probably true for other cyclic disulfides too. From naive MO-theory,[3,6] one expects the free energy of complex formation to become more negative as the dihedral angle of the disulfide bond (CSS/SSC) decreases.

It seems likely that the yields of monomer from the depolymerization process are determined by a balance between the free energy of polymerization of the free monomer disulfide and the difference in the free energy of complex formation between monomer and polymer. High yields were obtained for the small ring monomers ($p = 3, 4, 5$) where the relatively small dihedral angle (CSS/SSC) of the monomer disulfide bond should be an important factor in determining both the free energy of polymerization and the free energy of complex formation for the monomer. For the large size rings ($p = 6, 10$) small yields were obtained. In these cases it seems likely that the dihedral angle of the disulfide is not very far from 90°, and thus the difference in ΔG of complex formation is small. However, the free energy of polymerization may be numerically quite large because of interactions in the alkane part of the ring similar to those in the corresponding cycloalkane rings.

Experimental. Disulfide polymers $(-S(CH_2)_pS)_n$ were obtained by iodine (in aq. KI) oxidation of the corresponding dithiols (in petroleum ether). The resulting polymers were carefully washed with water, aq. $Na_2S_2O_3$, and again with water. In order to remove remaining traces of monomeric disulfide, the polymers were washed with large amounts of petroleum ether, and then stored at least over night in petroleum ether. The polymers were then washed once more with petroleum ether and dried on a filter paper.

Depolymerization. A small weighed sample of polymer (20–150 mg depending on monomer size) was mixed with an approximately twofold excess of solid iodine. For $p = 3, 4, 5$ small drops of liquid were formed immediately and a few minutes after mixing the whole sample consisted of an almost black liquid. For $p = 6, 10$ the mixture had to be heated gently, to *ca.* 70°C, to bring about the same change. After *ca.* 15 min, 10 ml of heptane (Fluka, for UV-spectroscopy) were added and the mixture was shaken for *ca.* 30 min.

Not all of the liquid dissolved in the heptane, since the amount of heptane was in general not sufficient to dissolve all the excess iodine. (However, for $p = 4, 5$ the remaining undissolved product disappeared slowly when the solution was treated with aq. $Na_2S_2O_3$.) When the shaking was completed a large excess of aq. $Na_2S_2O_3$ was added and the resulting mixture was shaken till all traces of iodine had disappeared. One or two ml of the heptane layer were diluted to a concentration suitable for UV-spectroscopy. In order to correct for remaining monomer in the polymer a similar amount of polymer was extracted with 10 ml heptane for approximately the same length of time as the above manipulations. The UV-spectra were run on a Cary SP 15 M.

The yields were calculated from the assumption that the UV-absorption at the disulfide absorption maximum was due solely to the monomeric disulfide. These absorptions were corrected for the monomer extracted from the polymer. The corresponding disulfide con-

Table 1.

	λ_{max} (mμ)	ε_{max}	% conversion
1,2-Dithiolane	330	179[a]	72
1,2-Dithiane	290	310[b]	92
1,2-Dithiepane	259	456[c]	81
1,2-Dithiacyclooctane	268	450[d]	4[e]
1,2-Dithiacyclododecane	263	450[d]	8

[a] Ref. 2. Values in the literature are ε_{max}= 147 (aq. ethanol) and ε_{max}= 142 (CH_2Cl_2).[9]
[b] Unpublished value. Lit. value log ε_{max} = 2.50 (methanol, cyclohexane).[10]
[c] The average of ε_{max}= 444 [7] and ε_{max}= 467 [11] (both values in ethanol).
[d] Assumed value. Typical for non-cyclic disulfides.
[e] The disulfide concentration was found to decrease slowly. The initial yield may have been 1 or 2 % higher.

Table 2.

Reaction product from $(-S-(CH_2)_3-S)_n$. 1,2-dithiolane.[a]

μ_{max}kK.	ε_{max}	μ_{max}kK.	ε_{max}
30.3	—	30.31	179
μ_{min}	ε_{min}	μ_{max}	ε_{min}
35.1	75	36.7	49

Reaction product from $(-S-(CH_2)_4-S)_n$. 1,2-dithiane.[b]

μ_{max}kK.	ε_{max}	μ_{max}kK.	ε_{max}
34.5	—	34.46	310
41.4	157	41.4	158
μ_{min}	ε_{min}	μ_{min}	ε_{min}
38.8	103	38.8	101
42.7	144	42.4	147

[a] Ref. 2.
[b] Unpublished values.

centrations were obtained using ε-values given in the literature (see Table 1).

In order to give an idea of the similarity between the UV-spectra obtained here and the UV-spectra of authentic disulfides, frequencies and ε-values of the maxima and minima of the UV-spectra obtained in this work are compared with the corresponding values from UV-spectra of authentic disulfides (because of lack of data this comparison was possible only for p= 3 and 4). The ε-values were calculated from the yields given in Table 1.

Synthesis of 1,2-dithiaheptane. 2.07 g of 1,5-pentane dithiol (Fluka) were dissolved in 10 ml petroleum ether. To this solution were added 10 ml aq. I_2,KI solution (3.23 g I_2, 3.30 g KI). The mixture was shaken till the iodine color had disappeared. The aqueous phase was removed, and the petroleum ether was distilled off at reduced pressure from the remaining mixture. 5.78 g I_2 were added to the residue and the reaction was allowed to proceed for *ca.* 1 h. Then 30 ml chloroform were added and the mixture was shaken for 15 min. Aq. $Na_2S_2O_3$ was added and the mixture was shaken till all the iodine color had disappeared. The chloroform layer was separated off and washed with aq. $Na_2S_2O_3$ and water (3 times 20 ml) and then dried over night with $CaSO_4$. The chloroform was distilled off at reduced pressure and the resulting raw disulfide (1.84 g) was distilled. Upon distillation a large part of the raw disulfide polymerized. Yield 0.48 g (23 % of the theoretical) n_D^{25}= 1.570 (lit. 1.570,[4] 1.569[7]).

1. Nelander, B. *Acta Chem. Scand.* **20** (1966) 2289.
2. Nelander, B. *Acta Chem. Scand.* **23** (1969) 2127, 2136.
3. Nelander, B. and Norén, I. *Acta Chem. Scand.* **26** (1972). *In press.*
4. Schöberl, A. and Gräfie, H. *Ann.* **614** (1958) 66.
5. Dainton, F. S., Davies, J. A., Manning, P. D. and Zahir, S. A. *Trans. Faraday Soc. Soc.* **53** (1957) 813.
6. Bergson, G. *Arkiv Kemi* **12** (1958) 233.
7. Field, L. and Barbee, K. B. *J. Org. Chem.* **34** (1969) 36.
8. Baltrop, J. A., Hayes, P. M. and Calvin, M. *J. Am. Chem. Soc.* **76** (1954) 4348.
9. Moreau, W. M. and Weiss, K. *J. Am. Chem. Soc.* **88** (1966) 204.
10. Kalff, H. T. and Havinga, E. *Rec. Trav. Chim.* **81** (1962) 282.
11. Smissman, E. E. and Sorensen, J. R. J. *J. Org. Chem.* **30** (1965) 4008.

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