Convenient Preparation of *cyclo*-Eicosasulphur (S_{20}) from Bis(η-cyclopentadienyl)(pentasulphido)titanium(IV)

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High-pressure liquid chromatographic analysis of stoicheiometric mixtures of $[Ti(cp)_2S_5]$ (cp = η-cyclopentadienyl) and SO_2Cl_2 in CS_2 solution has revealed the presence of S_{10}, S_{15}, S_{20}, and S_{25} in order of decreasing concentration. The compound S_{20} has been isolated in 8% yield and a reaction mechanism explaining its formation is proposed. An improved synthesis (88% yield) of $[Ti(cp)_2S_5]$ from $[Ti(cp)_2Cl_2]$ is also reported.

Homocyclic S_{20} is the largest sulphur ring whose structure is known from an *X*-ray diffraction study.[1] Larger sulphur rings have however been detected by high-pressure liquid chromatography (h.p.l.c.) in CS_2 solutions,[2,3] and polymeric sulphur is likely to contain a certain amount of large rings.[4] So far, S_{20} has been prepared in 40—80 mg amounts only, either from chlorosulphanes and sulphanes by condensation [1] or from liquid sulphur by quenching, extraction, precipitation, and recrystallization.[5] Both syntheses are laborious and, consequently, the chemical properties of S_{20} are practically unknown. Infrared and Raman spectra of solid S_{20} have however been reported,[5] and according to an *X*-ray diffraction analysis the S_{20} molecules form relatively flat non-planar rings of C_2 symmetry with bond lengths of between 202.3 and 210.4 pm.[1]

We here report the first convenient synthesis of S_{20} in gram amounts according to equation (1) (cp = η-C_5H_5). This reaction

$$[Ti(cp)_2S_5] + SO_2Cl_2 \longrightarrow \frac{1}{n} S_{5n} + [Ti(cp)_2Cl_2] \qquad (1)$$

was first studied by Schmidt *et al.*[6] who used it to prepare S_{10} (n = 2) in 35% yield.

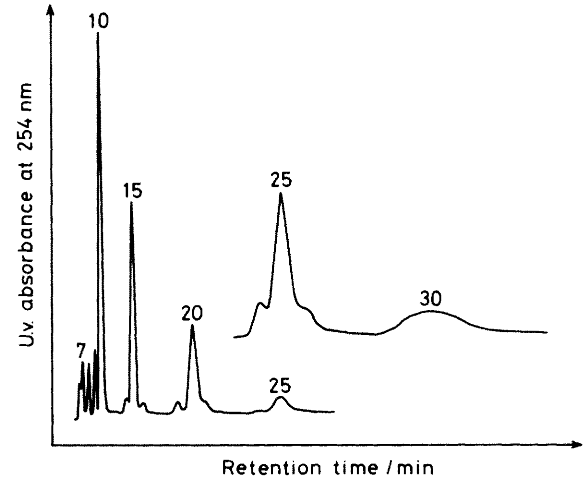


Figure. H.p.l.c. chromatogram of a stoicheiometric mixture of $[Ti(cp)_2S_5]$ and SO_2Cl_2 in CS_2 at 25 °C {after removal of most of the $[Ti(cp)_2Cl_2]$ formed} showing various homocyclic sulphur rings (the number of atoms per ring is indicated; for details see the Table). The enlarged section was recorded with six times increased sensitivity

Results

We have investigated stoicheiometric mixtures of $[Ti(cp)_2S_5]$ and SO_2Cl_2 in CS_2 solution at 0, 25, and 48 °C by h.p.l.c. in search of other rings S_{5n}. As the Figure and the Table demonstrate, the reaction mixture contains relatively high concentrations of S_{15} and S_{20} besides the main product S_{10} and small amounts of S_{25} and other rings S_m. The identification of the chromatographic peaks follows from the retention time which is a function of the ring size, as is the capacity factor.[2] Due to its low solubility in carbon disulphide, S_{20} can be recovered almost quantitatively [8% yield based on equation (1) with n = 4]; it has been characterized by Raman spectroscopy.

The product distribution listed in the Table and shown in the Figure is almost independent of the reaction temperature (0—48 °C) and of the concentrations of the starting materials. The amounts of S_{10} and S_{20} in the solution correspond to 'yields' of 31 and 10%, respectively. On *slow* addition of SO_2Cl_2, dissolved in CS_2, to the pentasulphide solution at 0 °C, however, increased amounts of S_{10} (51% 'yield') are formed at the expense of S_{20} and S_{25}. The amounts M listed in the Table were determined from the peak areas using calibration functions $A_m = f(c_m)$ empirically determined for each species using the pure compounds S_m in CS_2 solutions of similar concentrations; A_m = peak area of species S_m and c_m = concentration of species S_m. Details of the calibration will be published elsewhere.

During the course of this investigation we have also improved the synthesis of the starting material $[Ti(cp)_2S_5]$. According to Köpf and co-workers [7] $[Ti(cp)_2Cl_2]$ in acetone reacts with aqueous ammonium polysulphide at 20 °C according to equation (2); $[Ti(cp)_2S_5]$ (m.p. 201—202 °C) was

$$[Ti(cp)_2Cl_2] + (NH_4)_2S_5 \longrightarrow [Ti(cp)_2S_5] + 2\,NH_4Cl \qquad (2)$$

isolated in 43% yield based on $[Ti(cp)_2Cl_2]$.[7] However, ammonium polysulphide easily reacts with acetone to give the repulsively smelling 3,3,6,6-tetramethyl-1,2,4,5-tetrathiacyclohexane which forms colourless crystals of m.p. 98 °C.[8] We have therefore substituted acetone by chloroform and slightly changed the procedure, resulting in an increased yield (88%) of $[Ti(cp)_2S_5]$.

Table. Retention times (t), capacity factors (k), peak areas (A), and masses (M) of the sulphur rings S_m (m = 6—30) in an h.p.l.c. chromatogram of the products of reaction of $[Ti(cp)_2S_5]$ and SO_2Cl_2 at 25 °C

m	t/min	ln k	A/%	M/mg
6	1.42	0.005 634	—	—
7	1.52	0.126 5	ca. 4.5	ca. 94
8	1.80	0.424 0	3.0	68
9	2.10	0.667 5	4.0	92
10	2.36	0.839 2	26.7	616
12	2.87	1.108 9	0.4	6
14	3.48	1.357 8	1.9	—
15	3.79	1.464 0	21.6	—
16	4.23	1.597 6	1.9	—
19	5.76	1.958 7	3.3	—
20	6.45	2.086 8	17.2	201
21	7.05	2.186 2	—	—
24	9.34	2.494 7	11.8	—
25	10.28	2.598 1		—
26	11.50	2.718 1	—	—
30	17.10	3.166 2	3.8	—

Discussion

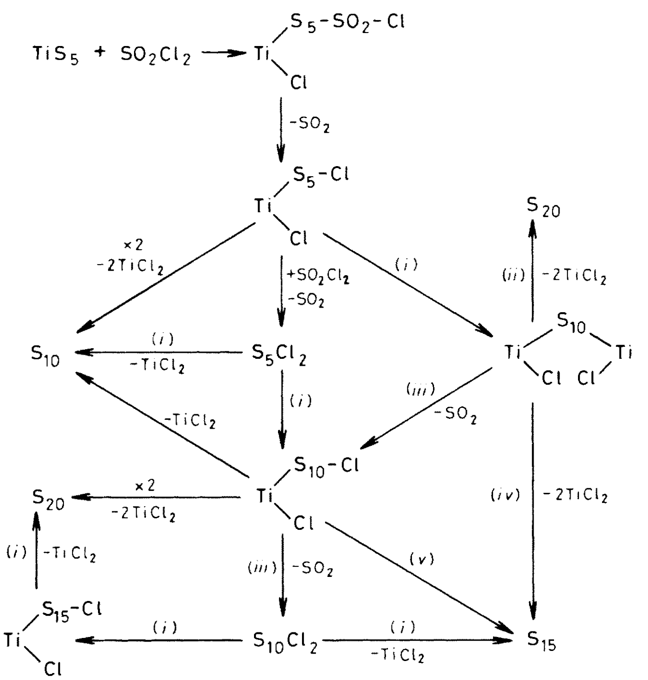
The preferred formation of sulphur rings S_{5n} (n = 2—6) in the reaction of $[Ti(cp)_2S_5]$ and SO_2Cl_2 can be understood by the series of reactions shown in the Scheme in which the cp ligands have been omitted for clarity. Two different routes exist for the formation of S_{5n} rings (*via* chlorosulphanes or without them), but most likely both routes are effective and free chlorosulphanes are intermediates of the above reaction. The compound S_5, which has not been observed, is obviously not an intermediate and, consequently, S_{10} is not formed by dimerization of S_5. This view is supported by the observation that addition of S_7 (2.81 g, 12.5 mmol) to a mixture of $[Ti(cp)_2S_5]$ (4.23 g, 12.5 mmol) and SO_2Cl_2 (1 cm^3, 12.5 mmol) prior to mixing did *not* result in an increased formation of S_{12}. If S_5 were an intermediate and the S_{5n} rings were formed by a series of ring-fusion reactions, *e.g.* $2\ S_5 \longrightarrow S_{10}$ and $S_5 + S_{10} \longrightarrow S_{15}$, considerable amounts of S_{12} should be formed at the expense of the rings S_{5n} when the very reactive S_7 is added to the reaction mixture: $S_5 + S_7 \longrightarrow S_{12}$.

In addition to the species discussed so far a number of rings S_m is formed in small concentrations in which m is not an integer which is a multiple of 5. These species may result from decomposition of the chain-like intermediates of type $R{-}S_{5n}{-}Cl$ [R = Cl or $(cp)_2TiCl$] according to equation (3). For

$$R{-}S_{5n}{-}Cl \longrightarrow S_m + R{-}S_{5n-m}{-}Cl \qquad (3)$$

$n > 1$ the splitting off of small rings S_m (m = 6—9) is possible and the remaining sulphur chain $R{-}S_{5n-m}{-}Cl$ will react with the intermediates of the Scheme discussed above leading to various small and large rings.

The isolation of S_{15} from the above reaction mixtures is in progress, and an extensive h.p.l.c. investigation of the reactions of $[Ti(cp)_2S_5]$ with chlorosulphanes, S_mCl_2 (m = 1—8), will be published elsewhere.



Scheme. cp ligands are omitted. (*i*) $+[Ti(cp)_2S_5]$; (*ii*) $+S_{10}Cl_2$; (*iii*) $+SO_2Cl_2$; (*iv*) $+S_5Cl_2$; (*v*) $+[Ti(cp)_2Cl(S_5Cl)]$

Experimental

Preparation of $[Ti(cp)_2S_5]$.—The compound S_8 (80 g) and concentrated aqueous NH_3 (33% by weight, 220 cm^3) were placed in a reaction bottle (2 l) and a medium stream of H_2S gas bubbled into the solution with stirring. To ensure a slight overpressure of H_2S and NH_3 within the bottle, the gas exit tube leading to a hood contained a cotton wad. Within 1 h the S_8 dissolved resulting in a warming of the red solution. After 1.5 h the weight gain amounted to 40 g [$2\ NH_3 + H_2S + \frac{1}{2}S_8 \longrightarrow (NH_4)_2S_5$]. The solution was then degassed for 10 min under a vacuum, and H_2O (150 cm^3) and $CHCl_3$ (1.5 l) followed by $[Ti(cp)_2Cl_2]$ (50 g) were added with vigorous stirring. After 20 h the black-red mixture was transferred quantitatively to a separation funnel (5 l), water (500 cm^3) was added, and repeated extraction by 700 cm^3 portions of $CHCl_3$ was performed until the red colour of the extracts became very faint. The combined extracts were filtered, the solvent completely removed under a vacuum, and the residue dried at 75 °C in a vacuum. Yield: 60 g (88%) $[Ti(cp)_2S_5]$. The purity (m.p. *ca.* 190 °C) of the product is sufficient for preparative work.

Preparation of S_{20}.—The compounds $[Ti(cp)_2S_5]$ (33.8 g, 100 mmol) and CS_2 (1.2 l, distilled from P_2O_5) were stirred for 10 min at 25 °C with exclusion of moisture, and a solution of SO_2Cl_2 (8 cm^3, 100 mmol, freshly distilled) in dry CS_2 (72 cm^3) was rapidly added with vigorous stirring. After 30 min the precipitated $[Ti(cp)_2Cl_2]$ was filtered off, the filtrate concentrated to a volume of 400 cm^3 at 70 °C bath temperature, followed by drying over $MgSO_4$ and cooling to −78 °C. The precipitate obtained after 7—10 d was isolated by rapid filtration of the cold solution and immediately extracted with CS_2 (50 cm^3) at 25 °C for 15 min with simultaneous crushing of the larger particles by a spatula. The crude product thus obtained was washed with CS_2 (40 cm^3) and then with 50-cm^3 portions of $CHCl_3$ (distilled from $CaCl_2$) until the solvent was colourless. Yield after drying in air: 1.24 g (8%) S_{20} as a yellowish powder occasionally contaminated by traces of S_{10} which can be removed by recrystallization from CS_2.

H.P.L.C. Analysis (*Figure*, *Table*).—The compound $[Ti(cp)_2S_5]$ (4.23 g, 12.5 mmol) and dry CS_2 (150 cm^3) were stirred for 10 min at 25 °C and a solution of SO_2Cl_2 (1 cm^3, 12.5 mmol, freshly distilled) in dry CS_2 (9 cm^3) was added with exclusion of moisture, resulting in an immediate colour change from dark red to orange and precipitation of $[Ti(cp)_2Cl_2]$. After stirring for another 30 min and filtration, the filtrate was concentrated to 50 cm^3. For h.p.l.c. analysis, 1 cm^3 of the solution was diluted with CS_2 (49 cm^3) and analysed by use of a Perkin-Elmer liquid chromatograph (series 2) comprising two pumps, a gradient system, magnetic mixer, Rheodyne injector (10 μl), Waters Radial-Pak C_{18} column (length 10 cm, inner diameter 8 mm, particle size 10 μm), Perkin-Elmer LC75 spectrophotometric detector (254 nm), and Hewlett-Packard 3390A integrator. A mixture of 60% (by volume) of methanol (distilled from $MgSO_4$), 33.3% cyclohexane (p.a.), and 6.7% ethanol (p.a.) was used as an eluant; flow rate 4 cm^3 min^{-1}.

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