Scheme 1.

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Derivatives of Thio- and Selenocarbonic Acids

I. An Adduct of Trithiocarbonate Ion and Carbon Disulfide

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The previously reported [1] formation of dialkyl triselenocarbonates from carbon diselenide, an alkyl halide and an oxygen base requires that an oxygen-selenium exchange takes place at the carbonate group. The restriction of this reaction to dimethyl sulfoxide (DMSO) and related

solvents might be due to the intervention of one or more highly solvent-sensitive intermediates. As part of a search for such intermediates the analogous system trithiocarbonate ion-carbon disulfide has now been studied in DMSO and in dimethyl formamide (DMF) by means of conductivity measurements and visible and infrared spectroscopy. The preliminary results of the three types of measurement show that a new species is formed, but attempts to trap this species, e.g. with alkyl halides, oxidizing agents or heavy metal ions, have so far been unsuccessful.

Experimental. Potassium trithiocarbonate (Ia) and sodium trithiocarbonate (Ib)[2] were purified by dissolving them in methanol containing a few percent of water and precipitating the crystalline dihydrates by adding 2-propanol. The precipitates were dried at room temperature and 0.2 mmHg. Since both salts are hygroscopic and sensitive to oxygen and carbon dioxide,[2] particularly when moist, they must be protected from the atmosphere during purification and measurements, and the solvents used must be deoxygenated. Equivalent weights were determined by titration with HCl, and the absence of the usual[2] contaminants, viz. perthiocarbonates, carbonates, and thiosulfates, was checked by means of IR and visible spectroscopy. E.W: (Ia) found: 110, calc. for $K_2CS_3,2H_2O$: 110; (Ib) found: 95, calc. for $Na_2CS_3,2H_2O$: 95. Visible absorption (water): (Ia and Ib) 503 nm, $\varepsilon = 36$; the maximum was displaced to 529 nm for Ia and 514 nm for Ib in DMSO (ε unchanged). IR* (KBr): (Ia) ca. 3300 (m-br), 1600(m), 920(sh), 900(s), 887(vs), 813(vw), 565(m-br), 511(m); (Ib) 3450(m-br), 3220(m-br), 1600(m), 918(vs), 820(vw), 520(m), 496(m), 420(m).

The optical density at 529 nm remained unchanged for a period of 3 h for a solution of Ia in DMSO, and in the same period no increase of the optical density at 434 nm (corresponding to an absorption maximum of the perthiocarbonate ion, cf. Ref. 3) was observed. Thus DMSO does not oxidize Ia. It was found, however, that DMSO oxidized the new species formed with carbon disulfide; dimethyl sulfide was evolved and the optical densities at the new absorption maxima decreased ca. 10 % during the first hour. It is therefore essential to carry out the measurements in DMSO rapidly after the mixing of the reagents.

* Abbreviations: br=broad, m=medium, s=strong, sh=shoulder, v=very, w=weak.

Infrared spectra were recorded on a Perkin-Elmer Model 337 grating instrument using either 0.025 mm BaF_2 cells (1050—760 cm^{-1}) or 0.05 mm KBr cells (1030—400 cm^{-1}); visible spectra were recorded on a Unicam SP-800 spectrophotometer. A Radiometer CDM2d instrument was used for the conductivity measurements, and the cell was calibrated by adjusting the observed values for a series of NaI solutions in DMSO to the values of Sears et al.[4]

Results and discussion. On progressive addition of carbon disulfide to a DMSO solution of Ia (concentration range $5 \times 10^{-3} - 4 \times 10^{-2}$ M) the 529 nm absorption disappeared and new maxima appeared at 458 nm (shoulder at 506 nm) and 553 nm. The optical densities at the two new maxima approached limiting values (log $\varepsilon_{458} = 2.78$, log $\varepsilon_{553} = 2.60$), which, within experimental error, were reached with a 6-fold excess of carbon disulfide. Simultaneously, the conductivity of the solution increased towards a limiting value. The rate of these changes appeared to be limited only by the rate of mixing of the reagents. Both types of measurements showed that the process could be reversed by removing the carbon disulfide in a stream of nitrogen. Thus the reaction is rapid and reversible.

The work of Sears et al.[4] indicates that the molar conductivities in DMSO of 1:1 electrolytes not containing excessively large ions vary less than 10 %. Therefore
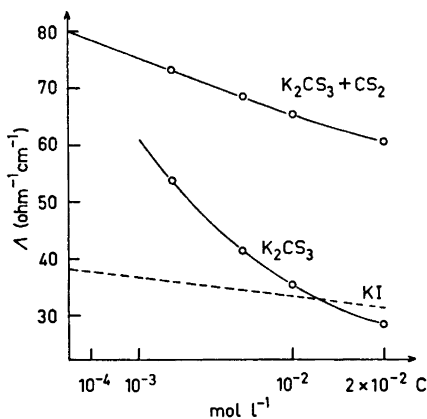

Fig. 1. Concentration dependence of the molar conductivity of K_2CS_3 in DMSO (25°) with and without added CS_2 ($C_{K_2CS_3}:C_{CS_2} = 1:10$).

a comparison of the molar conductivity of Ia with that estimated for KI at the same concentration by extrapolation from the results of Ref. 4 should give the approximate degree of dissociation of Ia. It was found (Fig. 1) that Ia behaved as a weak electrolyte with respect to both dissociation steps, whereas the addition of CS_2 led to the formation of a strong 2:1 electrolyte.

The concentration of the product species in a 6×10^{-3} M solution of Ia in DMSO with carbon disulfide added was calculated from the increase in the optical density at 553 nm and also from the increase in conductivity of the solution, assuming a linear relation between this quantity and the concentration of product. The values calculated according to the two methods were in all cases coincident within 1 % of the total concentration of Ia. Fig. 2 presents the calculated product concentration as a funtion of the ratio of stoichiometric concentrations, $f = C_{CS_2}/C_{K_2CS_3}$. The initial slope of the curve shows that a 1:1 reaction between Ia and carbon disulfide takes place, i.e. that a species with the composition $C_2S_5{}^{2-}$ is presumably formed, and the rapid approach to the limiting value indicates a rather large equilibrium constant for the formation of the adduct.
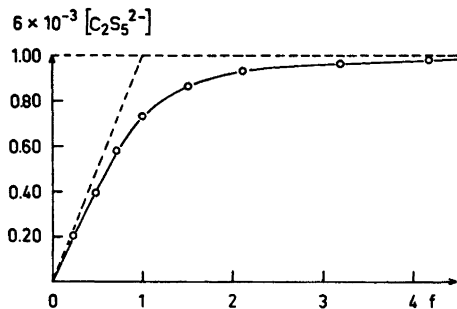
Since Ia is incompletely dissociated in DMSO a quantitative description of the observed equilibrium requires that three equilibrium constants be determined, viz. the first and second dissociation constants of Ia and the association constant for CS_2 and trithiocarbonate ion. Work to determine these constants is in progress.

It is also at present an unsolved problem whether the species $C_2S_5{}^{2-}$ is a molecular complex or a covalently bonded pentathiodicarbonate ion. The infrared spectrum of Ib in DMF with carbon disulfide added displays five absorptions that are not due to either reactant, namely at 1040(vs), 995(vs), 757(vs), 535(w) and 465(w) cm^{-1}. The last three absorptions were also observed for $Ia - CS_2$ in DMSO; this solvent is opaque in the region of the first two. Since the geometries of both possible types of structure can only be guessed at, the present information, lacking low frequency infrared as well as Raman data, does not allow a definite choice. As a working hypothesis, the covalent structure is assumed to be the more likely, since the observed absorptions differ significantly from those reported for the trithiocarbonate group coordinated to metal ions [5-6] and since the occurrence of a band at 757 cm^{-1} is compatible with the formation of a $C - S$ bond.

6×10^{-3} $[C_2S_5{}^{2-}]$

Fig. 2. Concentration of $C_2S_5{}^{2-}$ present in 6×10^{-3} M K_2CS_3 (DMSO, 25°) as a function of the ratio of stoichiometric concentrations, $f = C_{CS_2}/C_{K_2CS_3}$.

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