Chemistry of Carbon Sulfides

Jonathan Breitzer Final Seminar June 5, 2000

Carbon sulfides, neutral binary phases or charged species, are attractive materials because they come from plentiful feedstocks and are held together by robust bonds. The most fundamental stoichiometries for binary carbon sulfides are CS_2, which exists as a material as well as the monomer, and carbon monosulfide, CS, which is difficult to make in the laboratory although quite common extraterrestrially.[1] Others are C_3S_2,[2] C_3S_8,[3] C_4S_6 (three isomers),[4,5,6] and C_6S_{10} (Figure 1).[3]

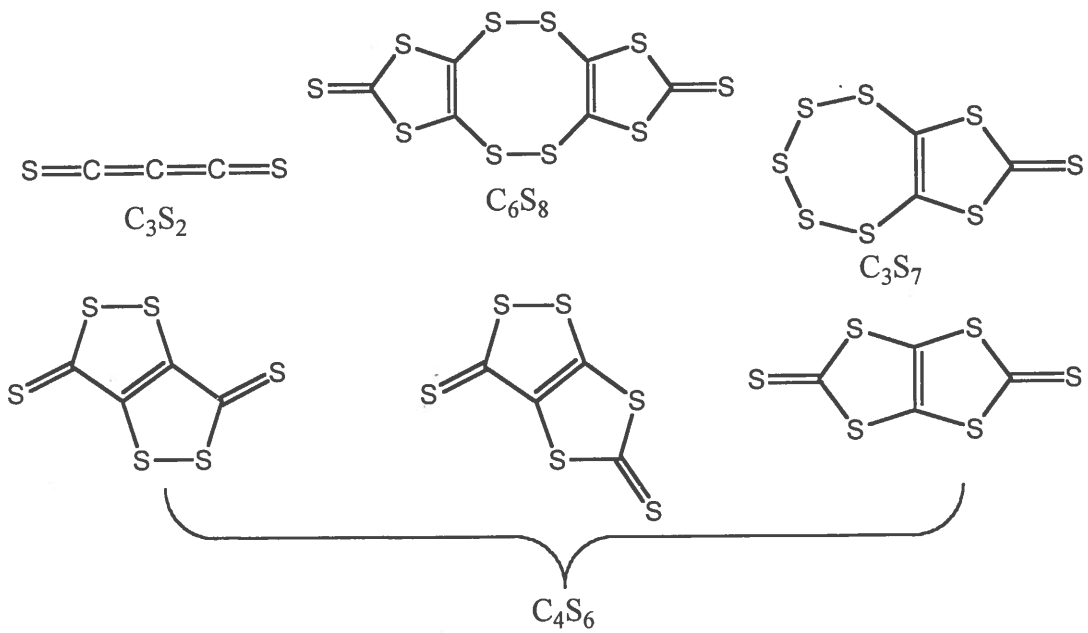

Figure 1

A great variety of structures are also found in anionic carbon sulfides. In particular, $dmit^{2-}$ ($C_3S_5^{2-}$), made from carbon disulfide,[7] is a source material for many other carbon sulfides. The organic derivatives of $dmit^{2-}$ have been studied,[8] and it is of considerable interest as a ligand for conductive and superconductive materials made from its coordination complexes.[9] Other carbon-sulfide anions are $C_4S_4^{2-}$ (the tetrathiosquarate anion)[10] and $C_8S_8^{2-}$,[11] a triplet radical species derived from $dmit^{2-}$.

Here, the fundamental properties of carbon sulfide anions are investigated. Two syntheses of tto^{2-}, one from C_2Cl_4 and the other from CS_2, are described. The presence of the tto^{2-} anion (tetrathiooxalate, $C_2S_4^{2-}$) as an intermediate in the formation of $dmit^{2-}$ from the reduction of CS_2 is suggested by conversion of tto^{2-} to $dmit^{2-}$ upon treatment with CS_2. The product was confirmed by preparing the titanocene derivative. Additionally, a ^{13}C NMR spectroscopic study using ^{13}C-enriched CS_2 confirmed the expected location of the carbon from the added CS_2 on the $dmit^{2-}$ product. CS_2 will also bind reversibly to one of the thiolate functionalities of $dmit^{2-}$ itself to form a monoadduct; this was initially suggested by a drastic

color change upon addition of CS_2 to $dmit^{2-}$. The thiolate and trithiocarbonate groups equilibrate in the presence of excess CS_2.

The free $dmit^{2-}$ anion, as the tetramethylammonium salt, was crystallographically characterized. This anion is extremely solvatochromic, exhibiting lower-energy absorptions in lower-dielectric solvents. The pK_a of $dmitH^-$, 5.31, shows $dmit^{2-}$ to be a much weaker base than other dithiolenes. A new coordination complex of $dmit^{2-}$, $[Ni_2(dmit)_3]^{2-}$ is prepared and characterized in solution and crystallographically. This is the first coordination complex of nickel and $dmit^{2-}$ in which the metal/ligand ratio is other than 1:2.

The electrochemical properties of $dmit^{2-}$ and a carbon sulfide derived from it, C_6S_8, were investigated. $Dmit^{2-}$ will comproportionate with its fully oxidized derivative, $(C_3S_5)_n$, to form $C_6S_{10}^{2-}$, which was crystallographically characterized. C_6S_8 and $C_6S_8^{2-}$ comproportionate to form $C_{12}S_{16}^{2-}$, which, unlike $C_6S_{10}^{2-}$, occurs in equilibrium with the $C_6S_8^-$ radical in THF solution. The thermodynamics of the process of $C_{12}S_{16}^{2-}$ splitting into $C_6S_8^-$ radicals was measured to be $\Delta H = 51.5 \pm 0.5$ kJ mol^{-1} and $\Delta S = 110 \pm 3$ J mol^{-1} K^{-1}.

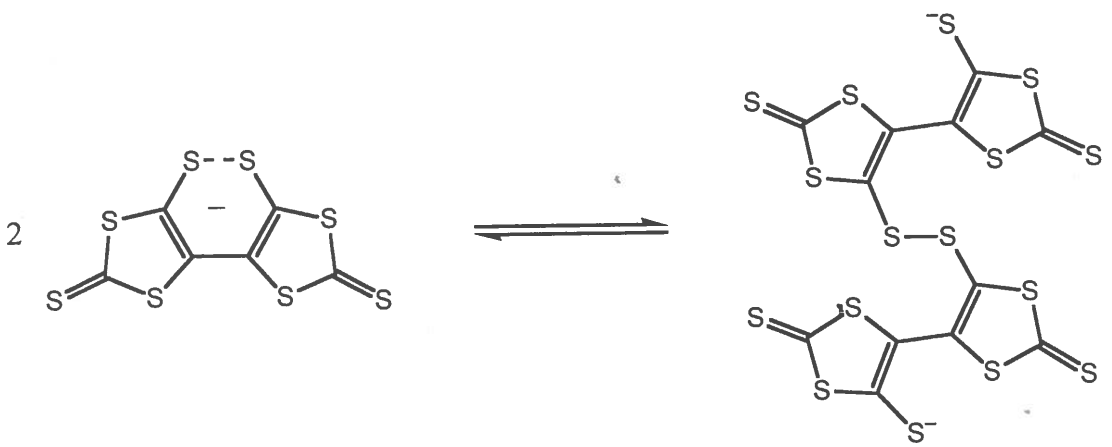

Figure 2

Third-order optical nonlinearities are present, in varying degrees, in all transparent materials. The technologically most relevant potential applications of materials possessing large third-order optical nonlinearities are photonic switches and bistable devices.[12] The third-order nonlinear optical susceptibilities of carbon sulfides, along with other sulfur-rich metal complexes, were measured using the z-scan technique with a 35 ps pulsed laser at 527.5 nm. The measurements were done in solution, which was continuously pumped through the sample cuvette to avoid heating. The susceptibilities of the molecules in solution was determined by subtracting the susceptibility of the solvent from that of the solution. The molecules which had the highest third-order optical nonlinearities were $C_6S_8O_2$ and $(Me_4N)_4[Zn_{10}(SPh)_{16}]$.

References

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