Relative Stabilities of Bis(triphenylmethyl) Polysulfides

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The relative stabilities of the bis(triphenylmethyl) di-, tri-, and tetrasulfides were studied by measuring their reactivity to oxygen at room temperature and measuring their thermal decomposition by EPR. About 25% of the disulfide in benzene solution was converted to the peroxide by reaction with air at room temperature for 8 h, whereas the tri- and tetrasulfides exhibited no reaction under these conditions. All of the polysulfides gave an EPR signal of the trityl radical when warmed in benzene solution. The temperatures of initial free radical appearance were 24, 75, and 66° for the di-, tri-, and tetrasulfides, respectively. Activation energies for the decomposition were also measured by EPR; they are 15, 80, and 30 kcal/mol for the di-, tri-, and tetrasulfides, respectively. The reason for this unusual order of stabilities is discussed.

Introduction

Although there is a report in the literature that bis(triphenylmethyl) disulfide in solution can react with oxygen to form bis(triphenylmethyl) peroxide,[1] no report exists with respect to the other bis(triphenylmethyl) polysulfides. The implication in Nakabayashi's paper[2] on the preparation of various bis(triphenylmethyl) polysulfides is that the higher sulfides are more stable than the disulfide. The only obvious way by which the disulfide might be predicted to be less stable than the higher polysulfides is a steric hindrance argument. There are other reasons, however, which might argue the reverse, namely, that the disulfide should be more stable than the higher polysulfides. The analogous bis(triphenylmethyl) peroxide is reasonably stable; furthermore, the strength of the S–S bond in polysulfides declines somewhat with length of the sulfur chain. The S–S bond dissociation energy in dimethyl disulfide is 67 kcal/mol[3] as compared to an average S–S bond energy of 36 kcal/mol for dimethyl tetrasulfide.[4] In the series of compounds, H_2S_2, H_2S_3, H_2S_4, H_2S_5, and H_2S_6 the average S–S bond dissociation energies in kcal/mol are 72, 64, 62, 62, and 62, respectively.[5]

In order to study the relative stabilities of the carbon–sulfur bond in bis(triphenylmethyl) polysulfides, the reactivities of the di-, tri-, and tetrasulfides were tested with respect to oxygen. The ease of thermal decomposition to form radicals was also studied using electron paramagnetic resonance.

Experimental Section

Bis(triphenylmethyl) Disulfide. The bis(triphenylmethyl) disulfide was prepared by condensation of triphenylmethylsulfenyl chloride with triphenylmethanethiol in a modification of the method described by Vorlander and Mittag.[6] A solution of approximately 4 g of triphenylmethanethiol dissolved in ~200 ml of hot 95% ethanol was placed in a large beaker and cooled to about 0° in an ice bath. A solution of 1.2 g of sodium hydroxide in 95% ethanol (25 ml) was then added. With further cooling and stirring, approximately 1 g of sulfuryl chloride was added to the solution. After the disulfide precipitate formed, it was filtered and washed successively with 95% ethanol and acetone. The bis(triphenylmethyl) disulfide melted with decomposition at 155–157° (lit. mp 155° dec). Purity was checked by thin-layer chromatography and infrared absorption.

Bis(triphenylmethyl) Trisulfide and Bis(triphenylmethyl) Tetrasulfide. Both compounds were obtained by the method of Nakabayashi.[2] The products were recrystallized several times from chloroform–methanol. Both compounds were light yellow crystals. The trisulfide melted at 146–147° (lit. mp 147–148°). The tetrasulfide melted at 147–149° (lit. mp 146–148°). Purity was checked by thin-layer chromatography and infrared spectroscopy.

Reaction of Bis(triphenylmethyl) Polysulfides with Oxygen. Approximately 0.5 g of bis(triphenylmethyl) disulfide was dissolved in 15 ml of dry benzene in a 50-ml two-necked flask equipped with a gas-inlet tube and vent. A stream of air was dried by passing it through a 45-cm column packed with silica gel. The air was then saturated with dry benzene and bubbled through the disulfide solution at room temperature. After about 2.5 h a small amount of white solid was noted on the sides of the reaction vessel. After about 5 h the solid was filtered, washed with CS_2, recrystallized from toluene, and dried under high vacuum. About 0.1 g of white crystals were obtained. The infrared spectrum (KBr) was identical with the Sadtler standard spectrum for bis(triphenylmethyl) peroxide. The crystals melted at 184–185° (lit. mp 185°). The tri- and tetrasulfides showed no reaction when treated similarly for 12 h.

EPR Spectra. EPR spectra were obtained with a Varian V-4502 100-kHz X-band spectrometer with 12-in. magnet and Fieldial MK II field regulation. Second-derivative presentation was used and the spectra were recorded on a Hewlett-Packard 15-in. X-Y recorder. Temperature was controlled by a Varian V-4547 cold gas apparatus and measured by means of a copper–constantan thermocouple.

The sample tubes consisted of thin-walled quartz tubing approximately 10 cm long and 4 mm in diameter which had been calibrated by volume per unit length. Known concentrations of about 10^{-2} M polysulfide in benzene were prepared on the vacuum line and the sample tubes were sealed off under vacuum.

In a typical procedure 4–6 mg of solid was weighed directly on a spatula and quantitatively transferred to the sample tube; then the spatula was reweighed and the sample weight was calculated by difference. The tube was then attached to the vacuum line and evacuated to a pressure of

about 10^{-6} mm. A small amount of dry benzene, which had been rendered free of dissolved oxygen by several successive deaerations, was then condensed in a ring just below the Pyrex-quartz graded seal. The liquid nitrogen level was lowered to the end of the tube and the benzene allowed to melt and flow down the sides of the tube, ensuring that any residual solid adhering to the inside of the constriction would be washed down. The tube was filled to the predetermined mark with benzene; then the liquid nitrogen level was raised to just below the 3mm constriction and the tube was sealed off and separated from the rest of the vessel. All samples were stored at $-10°$ until just prior to use.

Threshold temperatures for radical formation were determined by placing the sample in the microwave cavity and slowly increasing the temperature while sweeping the magnetic field until a resonance signal was noted on the recorder.

Decomposition rates were obtained by placing a previously decomposed sample into the cavity and equilibrating the cavity and sample to the desired temperature. The signal was then optimized to include only the four center lines of the radical. A fresh sample was then placed in the cavity and the spectrum immediately recorded. A sweep width of 2.5 G was used with a sweep time of 2.5 min. This enabled the four lines of interest to be scanned at the rate of one complete scan per minute. Scanning was continued until the increase in radical concentration, as evidenced by the size of the signal, appeared to be negligible. The elapsed time to a reference line of each spectrum was recorded. Rates were determined at several different temperatures each for bis(triphenylmethyl) di-, tri-, and tetrasulfides.

Results and Discussion

The results obtained by Blicke[1] in forming bis(triphenylmethyl) peroxide by oxygenating a solution of bis(triphenylmethyl) disulfide in benzene solution were reproduced. However, under identical conditions only starting materials could be recovered from oxygenation of bis(triphenylmethyl) trisulfide or bis (triphenylmethyl) tetrasulfide for 12 h. This confirms the *qualitative* observations that the disulfide is less stable than the other polysulfides. The formation of peroxide from the bis(triphenylmethyl) disulfide leads one to expect that homolysis of the carbon–sulfur bond has occurred with the concomitant production of triphenylmethyl and triphenylmethyldisulfur radicals.

Samples of the polysulfides prepared as described in the Experimental Section readily yielded the EPR spectrum of triphenylmethyl radical.[7] Because of the possibility of radicals of the type $Ph_3CS\cdot$, $Ph_3CSS\cdot$, etc., a careful search was made for different radical species. The only radical which could be detected by EPR was the triphenylmethyl free radical. A sample taken directly from an EPR tube which had been heated for several hours at $38°$ showed TLC spots corresponding to unreacted disulfide and sulfur and a very dark spot which did not move from the origin (assumed to be trityl dimer). If the tube is kept sealed, radical signals are lost after several months at room temperature and cannot be generated even on heating. This apparently corresponds to the known acid- or base-catalyzed isomerization of trityl dimer.[8] These results indicate that sulfur–sulfur bond cleavage is insignificant with respect to carbon–sulfur bond cleavage. This is not surprising in that the dissociation energy of the sulfur–sulfur bonds in dimethyl and diethyl disulfides are only slightly less than the carbon–sul-

fur bond dissociation energies, and with *tert*-butyl disulfide the two bond dissociation energies become approximately the same.[3]

Threshold temperatures for radical formation were determined for each of the polysulfides. The threshold temperature was taken to be the lowest temperature at which the triphenylmethyl radical could be detected. For the di-, tri-, and tetrasulfides the observed threshold temperatures were 24, 75, and 66°, respectively. The low threshold temperature for radical formation observed for the disulfide explains the ease of peroxide formation on reaction with oxygen at room temperature. Presumably, the tri- and tetrasulfides would also form peroxides if reacted with oxygen at or above their respective threshold temperatures.

If the decomposition is assumed to occur according to the net reaction

$$RS_xR \xrightarrow{k} 2R\cdot + S_x \qquad (1)$$
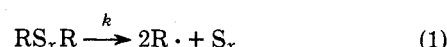
and the trityl radicals exist in rapid equilibrium with their dimer[9]

$$R_2 \overset{C}{\rightleftharpoons} 2R\cdot \qquad (2)$$

then the relation of trityl radical concentration, [R·], to the rate constant, k, is

$$[R\cdot] = [C(RS_xR)_0(1 - \exp(-kt))]^{1/2} \qquad (3)$$

where $(RS_xR)_0$ is the initial concentration of polysulfide and $[R\cdot] \ll [R_2]$. The peak heights of the EPR signal are proportional to [R·] and they were observed to follow this type of rate expression (e.g., a rapid rise at first followed by a gradual increase to a limiting value). Linearization of the first part of the plot could be obtained by plotting the square of the EPR peak height vs. time as as can be seen mathematically by squaring eq 3 and expanding the exponential.

$$[R\cdot]^2/C(RS_xR)_0 = kt - k^2t^2/2 + k^3t^3/6 + \ldots \qquad (4)$$

The first term of this expansion is accurate for small kt. Typical values observed for k in this study were 10^{-3} to 10^{-4} s^{-1}. However, obtaining the value of k from either 3 or 4 requires the measurement of the absolute value of the free radical concentration and accurate knowledge of C at the various temperatures employed.[10] Since this is rather tedious and subject to large errors we used the following method which does not depend on absolute concentrations or the value of the equilibrium constant. Since the radical concentration is proportional to the square root of the amount of polysulfide decomposed, the half-life, $\tau_{1/2}$, of the reaction was determined by the time taken for the EPR signal to attain $0.5^{1/2}$ of its final value. The rate constant for the first-order reaction was then obtained from $k = 0.693/\tau_{1/2}$. Runs at several temperatures for each of the polysulfides thus yielded rate constants from which the activation energies for decomposition were obtained by use of the Arrhenius equation. The values are 15, 80, and 30 kcal/mol for the di-, tri-, and tetrasulfides, respectively. There are at least two major possible sources of error in this measurement: (a) the lag in attainment of thermal equilibrium in the sample can give an error in the effective starting time; (b) disproportionation of the trityl radicals or isomerization of the trityl dimers will give an error in the final free radical concentration, although this is only a problem at the higher temperatures. Although the size of these er-

rors is difficult to estimate, which makes the absolute values quoted uncertain, the relative magnitudes are certainly in the order shown.

A number of reasons can be put forth to explain why the disulfide should be at least as stable as the tri- and tetrasulfides. As noted in the Introduction, the average S–S dissociation energy decreases with increasing sulfur chain length in polysulfides. The steric repulsion between the triphenylmethyl groups in bis(triphenylmethyl) disulfide should not be an important factor in decreasing its stability in that bis(triphenylmethyl) peroxide, where oxygen has a smaller atomic radius than sulfur, is a reasonably stable compound. A cyclic transition state, possibly involving d orbitals, would be expected to occur more readily in the higher polysulfides, with the result of easier decomposition. However, if it is assumed that the energy of the products is greater than the energy of the reactants, then the energy as well as the geometry of the transition state can be assumed to resemble that of the products.[11] The energy and geometry of the triphenylmethyl radical is the same for all the polysulfide decompositions. The other product formed by a carbon–sulfur bond cleavage is the S_2, S_3, or S_4 species. Of these, S_2 is the most stable on the basis that, when S_8 is heated, S_2 is the species formed almost exclusively. Since the products trityl plus S_2 are more stable than the other products, trityl plus S_3 and trityl plus S_4, it is reasonable to expect the transition state going to trityl plus S_2 to be lower than for the others. This argument can then be extended to explain the greater instability of the tetrasulfide over the trisulfide. Since the S_4 formed in the decomposition is a "dimer" of two S_2 units, the reaction might be expected to exhibit a lower transition state energy than the trisulfide decomposition. The foregoing argument assumes that the rate-determining step is the cleavage of either one or both carbon–sulfur bonds, and if it is the former, then subsequent breaking of the remaining carbon–sulfur bond must be rapid since no EPR signals attributable to sulfur-containing radicals were observed.

References and Notes

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COMMUNICATIONS TO THE EDITOR

On the Correction Term for Interactions between Small Ions in the Interpretation of Activity Data in Polyelectrolyte–Simple Electrolyte Mixtures

Sir: The activity of the added simple electrolyte in polyelectrolyte–simple electrolyte mixtures is an important quantity for the understanding of polyion–small ion interactions, and for the description of the properties of small ions in biological fluids and in ion exchangers. Experimental results for the activity of the simple salt have been compared with semiempirical expressions such as the "additivity rule",[1-3] or with a theoretical "limiting law" derived by Manning.[4] When experimental activity data are compared with the additivity rule, the measured values and the predicted activities were made to conform in the limit of no polyelectrolyte in the solution.[3,5,6] In the case of the limiting laws a similar *empirical* correction, suggested by Manning,[4,7] has been applied.[8-11] Typically, this correction can be expressed as[8]

$$\ln \gamma_{\pm} = \ln \gamma_{\pm}^{PM} + \ln \gamma_{\pm}^{MM} \qquad (1)$$

where $\gamma_{\pm}$, $\gamma_{\pm}^{PM}$, and $\gamma_{\pm}^{MM}$ denote respectively the mean molal activity coefficient of the added electrolyte, the contribution of the polyion–mobile ion interactions, and the contribution of the mobile ion–mobile ion interactions. Manning's limiting law only predicts $\gamma_{\pm}^{PM}$ because the work in charging the small ions is not considered in arriving at an expression for the free energy. It is the purpose of this communication to point out that the correction method given in eq 1, which leads to very satisfactory agreement of experimental data with the limiting law,[8-11] is also theoretically indicated by a comparison between Manning's limiting law and a result obtained for the total excess free energy obtained with a mode expansion method.[12-14]

It has been shown that both the cluster expansion method[15] and the mode expansion method[12] applied to polyelectrolyte solutions lead to an expression for the excess free energy of the form:[13,14,16]

$$F^{ex} = F_{PM}^{ex} + F_{MM}^{ex} \qquad (2)$$

where F^{ex}, F_{PM}^{ex}, and F_{MM}^{ex} respectively represent the ex-