Structure, Properties, and Thermodynamics of Poly(carbon dichalcogenides)

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Received July 29, 1987

ABSTRACT: Structural studies indicate that poly(carbon diselenide) has a head-to-head structure rather than the previously assumed head-to-tail structure. Thermodynamic properties and structure are investigated by using dual approaches for poly(carbon dichalcogenides): analysis of results for model compounds and quantum chemical calculations. Calculations using model compounds indicate that the head-to-tail structure has much lower energy than the head-to-head structure for poly(carbon dioxide), the energy difference is small for poly(carbon disulfide), and the head-to-head structure has much lower energy than the head-to-tail structure for poly(carbon diselenide)—which is consistent with the observation of the head-to-head structure for the latter polymer. The derived heat and free energy of polymerization (298 K) for formation of the amorphous head-to-tail polymer dramatically decreases in going from poly(carbon dioxide), H_p = 3.0 kcal/mol and G_p = 13.3 kcal/mol for gaseous CO_2, to poly(carbon disulfide), H_p = −7.0 kcal/mol and G_p = −3.4 kcal/mol for liquid CS_2. This heat of polymerization for liquid S=C=S is in good agreement with observation (−5.6 ± 1.9 kcal/mol). These results suggest that the high pressure typically used in the synthesis of poly(carbon disulfide) is required in order to obtain favorable kinetics but not to change the sign of the free energy of polymerization. Quantum chemical calculations provide that the head-to-tail structure has 38.8 kcal/mol lower energy than the head-to-head structure for poly(carbon dioxide), which is in agreement with the 38.5 kcal/mol energy difference derived by using experimental data on model compounds, and that the head-to-head structure has a 3.9 kcal/mol lower energy than the head-to-tail structure for poly(carbon disulfide), which is in agreement with the 4.0 kcal/mol energy difference derived by using experimental data of sulfides and disulfides.

I. Introduction

It is often assumed that, other contributions being equivalent, covalently bonded structures are thermodynamically preferred which provide heteroatomic bonding. For example, in addition reaction of a carbon dichalcogenide (X=C=X) it has been assumed[1,2] that the reaction product would have the head-to-tail connectivity of structure I, as opposed to the head-to-head connectivity of structure II.

$$(-X-C(=X)-X-C(=X)-)_n$$
I

$$(-X-C(=X)-C(=X)-X-)_n$$
II

This contention has been recently questioned by Iqbal et al.[3] in an examination of the poly(carbon diselenide) prepared by either ultraviolet or thermal polymerization of CSe_2. Extended X-ray absorption fine structure spectroscopy (EXAFS) and vibrational spectroscopy are consistent with structure II and are inconsistent with either structure I[1,2] or alternate structures[4-6] which have been previously proposed.

We will here examine experimental results which differentiate between structures I and II, refine the structural models, predict properties, and present thermodynamic arguments which could explain the preference of structure II for certain chalcogenides, but not for others. Understanding the structure of delocalized chalcogenide-based polymers is of increased interest because of the observation of superconductivity in polymers such as $(SN)_x$,[7,8] brominated $(SN)_x$,[7] $(Se)_x$,[9] and chalcogenide-containing charge-transfer complexes.[10-13] Superconductivity at high pressures has been claimed for poly(carbon diselenide)[5] but is now believed[14,15] to result from free selenium present in these samples.

II. Structure Analysis for Poly(carbon diselenide)

Whether or not $(CSe_2)_n$ results from the polymerization of CSe_2 strongly depends upon reaction conditions, which might reflect the lability of Se–Se bonds in the polymer structure. For example, polymerization of neat CSe_2 at 100 °C (external temperature of cell) and pressures of 4.5–5.5 kbar for about 15 h results in a mixture of free selenium and a carbon-containing metallic material of approximate composition $(CSe_{0.5})_n$.[14] On the other hand, for 5% CSe_2 solutions in dioxane or methylene chloride under about the same conditions or for room temperature, thermally induced, or photoinduced polymerization of neat CSe_2, a product is obtained[3,16,18] which has the composition $(CSe_2)_n$ and does not contain detectable free selenium.[3] A stability problem is clearly evident, since heating any of the latter reaction products at ~175 °C for 2 h results in the formation of free selenium.[3] The following discussion is restricted to the above-described $(CSe_2)_n$ polymer samples which do not contain detectable free selenium.

Support of structure II for $(CSe_2)_n$ is provided by a variety of measurements. The principal diagnostic lines in a resonance-enhanced Raman spectrum are a pair of broad, intense features at 1400 and 1475 cm^{-1}, which are assigned to a conjugated carbon–carbon bond,[19] and low-frequency vibrations at 244 and 290 cm^{-1}, which are assigned largely to Se–Se and C–Se stretching vibrations of a $(CSeSeC)_n$ backbone. The latter correspond to the Raman lines at, respectively, 214 and 262 cm^{-1} in $Se_2(C_6H_5)_2$. The principal diagnostic peaks in the infrared spectrum are relatively strong lines at 865 and 895 cm^{-1}, which are assigned to localized C=Se stretching modes in the polymer. A line having this assignment has been observed at 885 cm^{-1} for CSe_2 polymerized at ambient[2] and at 880 cm^{-1} for both CSe_2 solutions[15] and neat CSe_2[4] thermally polymerized at high pressure. A corresponding infrared line is observed at 920 cm^{-1} for 1,3-diselenole-2-selone.[20]

The X-ray diffraction pattern[3] consists of a strong halo at d = 2.87 Å and two weaker, broad reflections at 1.60 and 5.04 Å. There is no indication of scattering from either amorphous or crystalline free selenium. The large peak

0024-9297/88/2221-1832$01.50/0

half-widths (10° in 2θ for the strongest reflection using Cu Kα radiation) imply the absence of long-range structural periodicity.

EXAFS measurements[3] provide a more detailed view of the structure. As is true for the above-described Raman and infrared spectra, these results are consistent with structure II and inconsistent with structure I. Specifically, the EXAFS data for the selenium K edge provide 0.8 seleniums at a distance of 2.32 Å from each selenium. In contrast, there are no Se–Se covalent bonds in structure I. On the other hand, this result is in agreement with expected Se–Se bonding distance for structure II (2.29 Å from the structure determination of $Se_2(C_6H_5)_2$)[21] and the covalent coordination number of seleniums about selenium in structure II (N = 0.5). The EXAFS-determined covalent coordination number of carbons about selenium (N = 0.6) is in much better agreement with that expected for structure II (N = 1) than that expected for structure I (N = $^3/_2$). The corresponding EXAFS-determined bond distance between carbon and selenium (1.94 Å) is reasonably close to the average of the expected C=Se bond distance (1.85 Å from the structure of 1,3-diselenole-2-selone and 1.82–1.99 Å from the structures of other model compounds)[21-24] and the expected C–Se bond distance (1.93 Å from the structure of $Se_2(C_6H_5)_2$).[21] The EXAFS results of Kobayashi et al.[4-6] on the low-conductivity material obtained from the high-pressure polymerization of neat CSe_2 are consistent with the above-mentioned data. These authors obtain a Se–Se covalent bond distance of 2.35 Å, for which N = 0.7, as well as evidence for selenium covalently bonded to carbon.

For calculation of nonbonded selenium–selenium distances for structure II, we will use the EXAFS-determined[3] average selenium-to-carbon covalent bond distance (1.94 Å for both C=Se and C—Se, which is within the observed range[23,24] of bond distances for each of these bonds) and the EXAFS-determined Se–Se bond distance (2.32 Å). Literature determination of the C(sp^2)–C(sp^2) bond length in conjugated systems and the bond angle about C(sp^2) (1.45 Å and 125°, respectively, from the structure of *trans,trans*-1,3,5,7-octatetraene)[25] provides additional parameters. The Se–Se–C bond angle used is from the structure determination of $Se_2(C_6H_5)_2$, 106°,[21] and the Se—C=Se bond angle, 126°, is from the quantum chemical calculations in section IV for poly(carbon disulfide).

The thereby derived separation between seleniums which are bonded to the same carbon is 3.46 Å, corresponding to a theoretical coordination number of unity for structure II. This distance and coordination number are in agreement with the EXAFS-determined[3] separation of 3.44 Å and the coordination number of N = 1.4 for nearest-neighbor selenium atoms which are not covalently bonded together. It is relevant to note that trigonal selenium has an intrachain interatomic separation at 3.47 Å,[26] which is toward the short end of the broad range of the van der Waals diameters estimated for selenium (3.3–3.8 Å).[27,28]

Structural results for model compounds (including $Se_2(C_6H_5)_2$, $Se_2(C_6H_4Cl)_2$, and $Se_2(CH(C_6H_5)_2)_2$) provide a dihedral angle of 74.5–82° for the C—Se—Se—C fragment.[23] Similarly, structural results on unconstrained disulfides provide a value of 80–90° for this dihedral angle about the chalcogenide–chalcogenide bond.[28] Consequently, these results for model compounds suggest that structure II for $(CS_2)_n$ and $(CSe_2)_n$ should be nonplanar, which will be confirmed by MNDO calculations. Because of steric interactions, structure I for these polymers must also be nonplanar and helical.

Note that the sum of covalent Se to Se and Se to C coordination numbers from EXAFS is 1.4, which is in good agreement with the predicted value of 1.5 if one-half of the seleniums are —Se— and one-half are C=Se, which is true for both structures I and II. While the experimentally obtained covalent coordination numbers (N(Se to Se) = 0.8 and N(Se to C) = 0.6) exclude structure I (for which N(Se to Se) = 0 and N(Se to C) = 1.5), there are differences between these experimentally determined values and those for structure II (N(Se to Se) = 0.5 and N(Se to C) = 1). These differences likely reflect uncertainties in extracting coordination numbers from the EXAFS data, which are difficult to assess, but might also reflect some degree of structural deviation from perfectly regular structure II. While the EXAFS-determined coordination numbers are not determined with sufficient accuracy to exclude the presence of head-to-tail linkages admixed with head-to-head linkages, the best agreement between observed and calculated coordination numbers results by assuming the absence of any head-to-tail linkages. Some degree of interchain cross-linking might occur. For example, Se=C—C=Se groups in structure II might react with similar groups in neighboring molecules to produce two interchain Se—Se bonds and corresponding transformation of carbon—carbon single bonds into double bonds. If we assume that this reaction occurs to a significant extent, the agreement between the predicted and observed sum of covalent coordination numbers decreases. Also, such reaction cannot be so massive as to remove all C=Se, since this group is strongly observed in the infrared spectra. A similar cross-linking reaction has been proposed[6,29] for structure I, but in this case C=C bond formation cannot result and an unusual valence structure must therefore be assumed for the product. The coordination numbers from the EXAFS data are in disagreement with those expected for the two-dimensional structural model proposed for $(CSe_2)_n$ by Kobayashi et al.[4-6] This model contains seleniums which are each singly bonded to two other seleniums and doubly bonded to a carbon, for which we have found no precedent in model compounds.

III. Predictions from Model Compounds

Preference for either structure I or structure II could naturally occur for kinetic reasons. However, for chalcogenides for which one of these structures has a much lower energy than does the other, the kinetics of reaction is also generally expected to favor formation of this product. We will here use the thermodynamics of model compounds to calculate the difference in energy of structure I and structure II, as well as the heat and free energy of polymerization for X=C=X. These predictions will be compared with the results of our MNDO calculations, which also provide predictions of chain conformation. All of the thermodynamic quantities referred to for the polymers will be for an amount of polymer which contains a mole of carbon atoms.

The difference in heats of formation of structure II and structure I can be expressed by the following equation:

$$H_f[\text{XXCXCX}] - H_f[\text{XCXXCX}] = H_f[\text{RXXR}] + H_f[\text{RR}] - 2H_f[\text{RXR}] + H_c \quad (1)$$

where X is the chalcogenide, R is a hydrocarbon group, and CX denotes C=X. The first three terms on the right-hand side of eq 1 result from the assumption of bond energy additivity and the last term on this side of the equation corrects for deviations from such additivity, which depends upon the choice of R. The enthalpy difference H_f[RXXR] + H_f[RR] – 2H_f[RXR] roughly corresponds to the difference in energy of the sum of C–C and X–X bond

Table I
Predicted Differences in Formation Enthalpy and Gibbs Free Energy (kcal/mol at 298 K) for the Head-to-Head and the Head-to-Tail Structures before Correction for Deviations from Bond Energy Additivity[a]

X	R	ΔH_f(gas)	ΔH_f(liquid)	ΔG_f(gas)	ΔG_f(liquid)
O	CH_3	+18.9			
	C_2H_5	+22.2	+22.5		
S	C_6H_5	-4.0	-7.1		
	CH_3	-4.4		-3.8	
	C_2H_5	-4.0	-3.5	-3.6	-3.4
	C_3H_7	-4.0	-3.6	-3.6	-3.4
	C_4H_9	-3.8	-3.7	-3.4	
Se	C_6H_5	-19.4			

[a] The difference in formation enthalpy (ΔH_f) is H_f[RXXR] - $2H_f$[RXR] + H_f[RR] and the diffference in Gibbs free energy is G_f[RXXR] - $2G_f$[RXR] + G_f[RR]. As elsewhere in this paper, all energies are per mole of carbon atoms.

energies and two C–X bond energies. We will see that this difference strongly depends upon the chalcogenide X and provides the general trend for changes in the energy difference between structure II and structure I in going from O to S and to Se. Since heats of formation are available for a variety of oxygen-containing hydrocarbons which contain the detailed structural assemblies found in structures I and II, we will use these compounds to directly calculate both H_f[OOCOCO] and H_f[OCOOCO]. The deviation between the differences in these energies and H_f[ROOR] + H_f[RR] - $2H_f$[ROR] provides the correction factor H_c in eq 1 that is appropriate for a specified type of substituent (R, an alkyl or aryl hydrocarbon). Heats of formation of a more limited number of sulfur-containing compounds and only a couple of selenium compounds are available. However, trends (as a function of the selected chalcogenide) in the energy H_f[RXXR] + H_f[RR] - $2H_f$[RXR], combined with trends in deviations from simple bond-increment additivity, will permit conclusions concerning the energy difference between structure I and structure II for the sulfur polymers and the selenium polymers.

The calculated energy differences corresponding to the right-hand side of eq 1 are provided in Table I for several functionalities R. Except for the heat of formation of diphenyl sulfide and the selenium compounds, which are from ref 30 and 31, the heats of formation of the model compounds used for the Table I calculations are from Stull, Westrum, and Sinke.[32] Note in Table I that the head-to-tail structure is predicted to have a much lower energy than the head-to-head structure when the chalcogenide is oxygen. Also note that this predicted difference decreases in magnitude and changes sign in going to sulfur and has about the same magnitude, but opposite sign, for selenium as for oxygen. More specifically, the assumption of bond-energy additivity results in a predicted stabilization of the head-to-tail structure by about 21 kcal/mol for oxygen and the stabilization of the head-to-head structure for selenium by about the same amount. These predicted energy differences are expected to be relatively insensitive to the state (solid, liquid, or gas) in which the comparison is made. Also, the differences in Gibbs free energy of these structures is expected to be very close to the difference in enthalpy. These expectations are supported by the results in Table I.

The calculated heats of formation for structure I and structure II carbon dichalcogenide polymers are provided in Table II, where we also indicate the model compounds and method of calculation utilized. Except for the heat of fusion of dimethyl oxalate[33] and the heats of formation of the cyclic sulfur compounds,[34] the heats of formation of the model compounds are from Stull, Westrum, and Sinke.[32] The heat of sublimation for ethylene carbonate (17.1 kcal/mol) was estimated by using group increments.[27] Also the heats of vaporization of dimethyl carbonate (7.9 kcal/mol) and acetyl peroxide (12.3 kcal/mol) and the heats of fusion of diphenyl carbonate (4.8 kcal/mol) were estimated by using data for model compounds[32] and assuming group additivity. The heats of formation of the amorphous polymers are approximated by the heats of formation calculated from liquid-phase data for the model compounds. Calculated formation energies for the gas phase and the liquid phase are used to calculate the heat of formation of the amorphous polymers (last column in Table II), assuming a heat of fusion of 1.9 kcal/mol and a heat of vaporization of 4.2 kcal/mol for $(CO_2)_n$ and a heat of vaporization of 6.6 kcal/mol for $(CS_2)_n$. The above heat of fusion was obtained from the heat of fusion of dimethyl oxalate (5.0 kcal/mol)[33] after subtracting an additive increment of 0.6 kcal/mol for each methyl.[27] The above heats of vaporization correspond, respectively, to the difference in heats of vaporization of acetic anhydride and

Table II
Heats of Formation (kcal/mol at 298 K) of Structure I and Structure II Poly(carbon dichalcogenides)[a]

calculation method	H_f (state of model compd)[b]	H_f for amorphous polym
Structure I Poly(carbon dioxide)		
H_f[$H_3COCOOCH_3$] - H_f[H_3COCH_3]	-94.7 (g)	-98.9
H_f[$H_5C_2OCOOC_2H_5$] - H_f[$H_5C_2OC_2H_5$]	-97.2 (l)	-97.2
H_f[$H_5C_6OCOOC_6H_5$] - H_f[$H_5C_6OC_6H_5$]	-88.4 (s)	-86.5
	-87.6 (l)	-87.6
H_f[$H_3CCOOCOCH_3$] - H_f[H_3CCOCH_3]	-89.8 (l)	-89.8
	-85.6 (g)	-89.8
H_f[$H_3CCOOCOCH_3$] - H_f[$H_3CCOCOCH_3$] + $^1/_2$(H_f[$H_3CCOCOCH_3$] - H_f[H_3CCH_3])	-88.4 (g)	-92.6
H_f[$H_5C_6COOCOC_6H_5$] - H_f[$H_5C_6COC_6H_5$]	-94.8 (s)	-92.9
H_f[—$CH_2OCOOCH_2$—] - H_f[—$CH_2CH_2OCH_2CH_2$—] + $^1/_3H_f$[cyclohexane]	-88.4 (g)	-92.6
Structure II Poly(carbon dioxide)		
$^1/_2$(H_f[$H_3CCOOOCOCH_3$] - H_f[$H_3CCOCOCH_3$]) + H_f[$H_3CCOCOCH_3$] - H_f[H_3CCOCH_3]	-44.9 (g)	-49.1
	-48.5 (l)	-48.5
$^1/_2$(H_f[$H_3CCOOOCOCH_3$] - H_f[H_3CCH_3])	-47.7 (g)	-51.9
$^1/_2$(H_f[$H_5C_2COOOCOC_2H_5$] - H_f[$H_5C_2C_2H_5$])	-56.4 (l)	-56.4
$^1/_2$(H_f[$H_5C_6COOOCOC_6H_5$] - H_f[$H_5C_6C_6H_5$])	-58.9 (s)	-57.0
Structure I Poly(carbon disulfide)		
H_f[—$CH_2SCSSCH_2$—] - H_f[—$CH_2CH_2SCH_2CH_2$—] + $^1/_3H_f$[cyclohexane]	21.0 (g)	14.4

[a] Energies are per mole of carbon atoms. Gas (g), liquid (l), or solid (s).

acetone[32] and the heat of vaporization of carbon disulfide.[32] Errors in these estimates will not have a substantial effect on the results of the present calculations.

Since the heats of formation could not be found in the literature for noncyclic compounds which include the -SCSS- linkage, it was necessary to use the heat of formation of the cyclic compounds $-CH_2SCSSCH_2-$ and $-CH_2CH_2SCH_2CH_2-$ for evaluating the heat of formation of structure I $(CS_2)_n$. Because of the possible effect of ring strain on such calculations, one could worry about the reliability of the resulting estimate of heat of formation of $(CSe_2)_n$. However, the calculation method involves the difference in heats of formation of two cyclic compounds, so ring strains will at least partially cancel. Moreover, the reliability of this calculation using cyclic molecules is supported by the analogous calculation for $(CO_2)_x$, which provides a formation enthalpy that does not significantly differ from that calculated by using the appropriate noncyclic reference molecules (Table II).

The results shown in Table II provide a heat of formation in the glassy state of -52.6 ± 4.0 kcal/mol for $(OOCOCO)_n$ and -91.1 ± 3.4 kcal/mol for $(OCO)_n$, where the indicated standard deviations reflect only the scatter of calculated values and each result is per mole carbon. These results indicate that structure I is much more stable than structure II for the carbon dioxide polymer.

The formation free energy is greater than the formation enthalpy of structure I $(CO_2)_x$ by an amount which is obtained from the following approximations:

$$G_f[I] - H_f[I] = G_f[H_3CCOOCOCH_3] - G_f[H_3CCOCH_3] - H_f[H_3CCOOCOCH_3] + H_f[H_3CCOCH_3]$$

and

$$G_f[I] - H_f[I] = G_f[H_5C_6OCOOC_6H_5] - G_f[H_5C_6OC_6H_5] - H_f[H_5C_6OCOOC_6H_5] + H_f[H_5C_6OC_6H_5]$$

From available formation enthalpies and formation free energies for these model compounds,[32] the first equation yields values for $(G_f[I] - H_f[I])$ of 8.2 kcal/mol in the gaseous state and 10.1 kcal/mol in the liquid state and the last equation yields 11.9 kcal/mol in the solid state. Since our derived value of $H_f[I]$ is -91.1 kcal/mol for amorphous structure I $(CO_2)_x$, the above liquid-phase value of $(G_f[I] - H_f[I])$ yields $G_f[I]$ = -81.0 kcal/mol in the amorphous state at 298 K. Since the free energy difference between structure II and structure I is approximately equal to the enthalpy difference for these structures ($H_f[II] - H_f[I]$ = 38.5 ± 5.2 kcal/mol, from the results in Table II), we obtain from the formation free energy of structure I that $G_f[II]$ = -42.5 kcal/mol in the amorphous state.

By use of the literature value[32] for the gas-phase (298 K) formation energies of CO_2, the heat and Gibbs free energy of polymerization of gaseous CO_2 to form structure I $(CO_2)_x$ in the amorphous state are $H_p[I]$ = 3.0 kcal/mol and $G_p[I]$ = 13.3 kcal/mol. The entropy change in formation of amorphous structure I poly(carbon dioxide) is then $(H_p[I] - G_p[I])/T$ or -34.6 kcal/(mol K). The values of H_p and G_p for structure II are 38.5 kcal/mol less favorable for reaction than those for structure I. Both sets of values provide the expected conclusion that such polymerization reactions of gaseous CO_2 cannot occur at ambient pressure.

Since the heat of formation of liquid CS_2 is 21.37 kcal/mol,[32] we predict from the results in Table II that the heat of polymerization of liquid CS_2 to form amorphous structure I $(CS_2)_n$ is -7.0 kcal/mol. This derived value is in good agreement with the experimentally derived difference in formation enthalpy (298 K and ambient pressure) between high-pressure-polymerized CS_2 and liquid CS_2[35] (-5.6 ± 1.9 kcal/mol).

We next need to evaluate the difference in formation enthalpy and formation free energy of amorphous structure I poly(carbon disulfide). This free energy difference is denoted $TS_f[SCS]$, where S_f is the formation entropy relative to the standard state of the elements and T is the reference temperature (298 K). The above free energy difference is calculated from the corresponding quantity for structure I poly(carbon dioxide) by correcting for the change in TS_f upon replacing —S— by —O— and replacing =S by =O in model compounds. Specifically, we obtain

$$TS_f[SCS] = TS_f[OCO] + TS_f[H_3CSCH_3] - TS_f[H_3COCH_3] + \tfrac{1}{2}(TS_f[S{=}C{=}S] - TS_f[O{=}C{=}O])$$

From the difference of the above-derived formation heat and formation free energy for amorphous structure I poly(carbon dioxide) (-91.1 and -81.0 kcal/mol, respectively), we obtain that $TS_f[OCO]$ is -11.1 kcal/mol for T = 298 K. The remaining terms in the above approximation for $TS_f[SCS]$ are obtained from differences in formation enthalpy and formation free energy for the model compounds in the gas phase,[32] since liquid-phase differences are not available for all of the model compounds. In using the gas-phase differences, rather than the liquid-phase differences, the approximation made is that the entropy change in vaporization of poly(carbon disulfide) is the same as the entropy change on vaporization of poly(carbon dioxide), which should be a good approximation. The thereby calculated $TS_f[SCS]$, which equals $H_f[I] - G_f[I]$, is +2.2 kcal/mol.

Using $H_f[SCS]$ = 14.4 kcal/mol, from Table II, we obtain $G_f[SCS]$ = 12.2 kcal/mol. Combining this value with the free energy of liquid S=C=S (15.56 kcal/mol),[32] we obtain that the free energy change at 298 K on polymerization of liquid carbon disulfide ($G_p[I]$) to form amorphous structure I is -3.4 kcal/mol. The corresponding entropy change on polymerization of liquid carbon disulfide calculated from our derived $(H_p - G_p)/T$ is -12 cal/(mol K). From the heat and free energy of formation of gaseous CS_2,[32,37] the heat and free energy of polymerization of gaseous CS_2 to form amorphous structure I poly(carbon disulfide) at 298 K are -13.6 kcal/mol and -3.8 kcal/mol, respectively. This provides an entropy change of -32.8 cal/(mol K) for the polymerization of gaseous CS_2 to form amorphous structure I poly(carbon disulfide). This entropy change for polymerization of gaseous CS_2 is nearly equal to our previously calculated entropy change of -34.6 cal/(mol K) for polymerization of gaseous CO_2 to form amorphous structure I poly(carbon dioxide). These calculated entropy changes for polymerization of gaseous CO_2 and gaseous CS_2 are reasonably close to the experimentally determined entropy changes for the polymerization of gaseous chloral (-45 ± 7 cal/(mol K)), gaseous fluoral (-44.7 cal/(mol K)), and gaseous formaldehyde (-40.4 and -41.6 cal/(mol K)), where the polymerization product is either partially crystalline (chloral and formaldehyde) or amorphous (fluoral).[36]

The calculations of Table I from eq 1 and the more accurate results of Table II both predict that structure I is much more stable than structure II for the carbon dioxide polymer. However, since the model compounds of Table I do not include important intergroup interactions that are included in the model compounds of Table II, $H_f[II] - H_f[I]$ obtained in Table I is about 17 kcal/mol lower than the 38.5 ± 5 kcal/mol difference calculated from the results in Table II.

One can hypothesize that the magnitude of this discrepency (corresponding to the correction factor H_c in eq

1) could dramatically decrease on going from oxygen to sulfur and selenium, since the Pauling electronegativity[38] of carbon (2.5) is very different from that of oxygen (3.5) but is close to those of sulfur (2.5) and selenium (2.4). Whatever the explanation, the MNDO calculations will support the conclusion that H_c is much smaller for sulfur than for oxygen. Since the Table I results predict very little energy difference between structures I and II for poly(carbon disulfide), the correction factor for intergroup interactions could make structure I lower in both enthalpy and free energy than structure II. However, since the Table I results predict such a large thermodynamic preference for structure II poly(carbon diselenide), this more favorable energetics is unlikely to be reversed by correction for intergroup interactions.

IV. Predictions from Quantum Chemical Calculations

The conclusions of the last section, which are based entirely on the analysis of results for model compounds, are supported in this section by semiempirical quantum chemical calculations. Since the introduction of the MNDO (modified neglect of diatomic overlap) method by Dewar and co-workers[39] in 1977, this semiempirical method has been applied to a large number of organic molecules with fairly good results in predicting the geometries and heats of formation. We have used MNDO (MOPAC Version 1.23 from the Quantum Chemistry Program Exchange, Indiana University (QCPE)) to predict geometries and heats of formation for carbon disulfide oligomers and poly(carbon disulfide). It has been shown that MNDO is quite successful in predicting the geometries of neutral S_n molecules.[40,41] Recently, Dewar et al.[42] have developed a new general-purpose quantum mechanical molecular method called AM1 (Austin Model 1). This method overcomes some of the major weaknesses of MNDO, in particular the failure to reproduce hydrogen bonds. We applied AM1, using AMPAC Version 1.0 from QCPE, to the carbon dioxide oligomers and polymer, since this method gives better heats of formation for oxygen-containing molecules than MNDO. AM1 is not yet parameterized for sulfur.

MNDO and AM1 calculations were performed for the head-to-tail molecules $H_3C-(XCX)_n-CH_3$ and the head-to-head molecules $H_3C-(XXCXCX)_n-CH_3$ (X = S or O) with n increasing from 1 to 4. The heat of formation (ΔH, per mole carbon) for the head-to-tail and head-to-head polymers were then derived from the change in heat of formation for n increasing from 3 to 4. In each case the structure utilized for the ΔH calculations corresponded to the calculated energy minima. The calculated change in formation energy (per mole of carbon) for n going from 3 to 4 differed at the most by 0.9 kcal/mol from the change in ΔH for n increasing from 2 to 3, suggesting that the oligomers have sufficient length to adequately represent the formation energy for the high polymers.

The accuracy of absolute heats of formation by MNDO and AM1 is known to be quite low for both oxygen- and sulfur-containing compounds. Specifically, if the experimentally evaluated differences in gas-phase formation energies tabulated in Table II are compared with the corresponding energy differences from the quantum chemical calculations on the same compounds (MNDO for the sulfur compositions and AMI for the oxygen compositions), the theoretically derived differences are systematically too high by an average of 7.5 kcal/mol for oxygen and 5.9 kcal/mol for sulfur. Since the energy differences for the model compounds in Table II contain the same –X– and –CX– contributions as in the poly(carbon dichalcogenides), the reliability of the AMI and MNDO calculated heats of formation for poly(carbon dichalcogenides) can be improved by subtracting, respectively, either 7.5 kcal/mol (oxygen) or 5.9 kcal/mol (sulfur) from the heats of formation for the polymers which were derived from the quantum chemical calculations.

Directly using only the results of the quantum chemical calculations, the heat of formation for the head-to-tail poly(carbon dioxide) is predicted to be lower than that of the corresponding head-to-head polymer by 38.8 kcal/mol. This result is in excellent agreement with the 38.5 kcal/mol energy difference obtained in section II by using only experimentally derived heats of formation of model compounds. The difference in formation energy for structure I and structure II poly(carbon disulfide) contains greater uncertainty because of the lack of experimental heats of formation for model compounds which contain the intergroup interactions present in the head-to-head polymer (structure II). Nevertheless, despite the resulting uncertainties in using the Table II results, the quantum chemical calculations predict that the head-to-head polymer is more stable than the head-to-tail polymer by 3.9 kcal/mol. This stabilization energy is in good agreement with the 4.0 kcal/mol energy difference derived from the gas-phase results in Table I. This agreement suggests that, in contrast with the case for poly(carbon dioxide), the term H_c in eq 1 is near zero for poly(carbon disulfide). Also, this result supports the approximation that H_c can be neglected in the evaluation of the structure I – structure II energy difference for poly(carbon diselenide) (Table I).

Note that the above energy differences result directly from the quantum chemical calculations and are independent of the previously mentioned corrections for errors in the determination of absolute formation energies. After applying these energy corrections (–7.5 kcal/mol from AM1 for poly(carbon dioxide) and –5.9 kcal/mol from MNDO for poly(carbon disulfide)), the calculations yield the following gas-phase heats of formation: –80.5 kcal/mol for the head-to-tail poly(carbon dioxide) (compared with –89.3 kcal/mol from Table II), –41.7 kcal/mol for the head-to-head poly(carbon dioxide) (compared with –46.3 kcal/mol from Table II), 24.5 kcal/mol for the head-to-tail poly(carbon disulfide) (compared with 21.0 kcal/mol from Table II), and 20.6 kcal/mol for the head-to-head poly(carbon disulfide). While the above agreement between these formation energies calculated by two different methods is about as good as can be expected, the formation energies from the quantum chemical calculations are consistently higher than those derived from the heats of formation of model compounds.

Neglecting any difference between the enthalpy of vaporization of poly(carbon disulfide) and CS_2, the heat of polymerization of liquid CS_2 to form amorphous poly(carbon disulfide), derived from the quantum chemical calculations and the observed[32] heat of formation of gaseous CS_2, is –3.4 kcal/mol for formation of structure I and –7.3 kcal/mol for formation of structure II. These results again suggest that the heat of polymerization of carbon disulfide at atmospheric pressure should be exothermic. Also, these results are reasonably consistent with both the experimentally derived heat of polymerization of liquid CS_2 (-5.6 ± 1.9 kcal/mol)[35] and the heat of polymerization for formation of structure I (–7.0 kcal/mol) derived from data on model compounds (Table II).

The optimized geometries for the longest oligomers (n = 4) can be used to predict the geometries of the polymer repeat units for structure I and structure II. Table III lists the predicted bond lengths, bond angles, and dihedral angles for the polymers. These parameters were derived

Table III
Predicted Geometries for Polymer Repeat Units from Quantum Chemical Calculations[a]

	O	S		O	S
Structure I			Structure II		
Bond Distances, Å			Bond Distances, Å		
$C{=}X_2$	1.214	1.536	C=X	1.218	1.545
$X_1{-}C$	1.371	1.700	X—X	1.298	1.923
			X—C	1.400	1.700
Bond Angles, deg			C—C	1.498	1.490
$X_1{-}C{-}X_1$	105	103			
$C{-}X_1{-}C$	118	112	Bond Angles, deg		
$X_1{-}C{-}X_2$	128	128	$X_1{-}X_2{-}C$	113	110
			$X_1{-}C{-}C$	110	110
Dihedral Angles, deg			$X_2{-}C_1{=}X_3$	120	126
$X_1C{-}X_1C$	-153	-151	$C_2{-}C_1{=}X_3$	130	123
$X_2C{-}X_1X_1$	180	180			
			Dihedral Angles, deg		
			CX—XC	-90	-100
			XC—CX	-180	-90
			XX—CC	-173	-165
			$X_3C_1{-}C_2X_4$	180	-100

[a] The chalcogenides and carbons connected by double bonds are $X_2{=}C$ in structure I and $X_3{=}C_1$ and $X_4{=}C_2$ in structure II. Singly bonded chalcogenides are X_1 in structure I and X_1 and X_2 in structure II. Atomic subscripts are eliminated when the indicated interatomic bonds uniquely specify a structural parameter.

from the central part of the longest MNDO and AM1 optimized oligomer. The end effect from the terminal methyl group on the geometry of the center of the molecule can be neglected for $n = 4$.

Not surprisingly, structure I can best be described as a simple helix for both the sulfur and the oxygen polymers. The dihedral angle in the backbone is very similar for both chalcogenides. Structure II is also predicted to be a helix. However, the twist is more severe than in structure I. The helix arises principally for the oxygen polymer from the CO–OC dihedral angle, which is about 90°. The equivalent dihedral angle in the sulfur polymer is also close to 90°. This prediction is in fair agreement with the angle found in unconstrained disulfide.[43] In addition, the SC–CS dihedral angle is predicted to be 90°, leading to a severely twisted helix.

V. Discussion

Bolduan et al.[44] have measured the temperature-pressure boundary curve for the appearance of a black product which they suggested to be poly(carbon disulfide). An initially red material formed at high pressure (70–80 kbar at room temperature), which faded to an extent reversibly upon decreasing pressure and became irreversibly black in appearance at higher pressures (above 90 kbar). The boundary on the pressure–temperature diagram where Bolduan et al.[44] see this product extrapolates to the region of the pressure–temperature diagram where Butcher et al.[45] identified formation of poly(carbon disulfide). The curve which describes the initial formation of the black product has a negative slope (-2.8 K/kbar). If this curve were basically determined by the equilibrium formation of poly(carbon disulfide), then one would conclude, using the Clausius–Clapeyron equation ($dT/dP = TV_p/H_p$), that the heat of polymerization (H_p) of carbon disulfide is positive, since the volume change on polymerization (V_p) is negative. Such a conclusion is contrary to the sign of the heat of polymerization which is observed[35] and calculated by using the heats of formation of model compounds. Hence, if the latter results are correct, either the pressure–temperature curve measured by Bolduan et al.[44] is not determined by equilibrium polymerization of CS_2 to form poly(carbon disulfide) or crystal strain effects for the initial formation of poly(carbon disulfide) in the monomer crystal phase are sufficient at low conversions to effectively change the sign of H_p. In light of the high strain energy that this would require and the associated likelihood of phase separation, the former explanation appears more likely.

The heat of fusion of CS_2 (1.05 kcal/mol)[37] is too small to change the sign of the measured heat of polymerization of liquid CS_2, so this aspect will not effect the above arguments. Relevant for the sign of V_p, the density reported[38] at room temperature for poly(carbon disulfide) provides a volume of 40.3 cm^3/mol, which is much less than either the molar volume of liquid CS_2 (60.4 cm^3/mol) or the crystalline volume[46] extrapolated at atmospheric pressure to room temperature (59.0 cm^3/mol).

Based on the above arguments, a kinetic origin is suggested for the negative slope of the pressure–temperature boundary curve for reaction of CS_2. Since the molar volume of polymer is significantly lower than that for the monomer, it is reasonable to assume a negative activation volume for polymerization. If the activation energy is positive, which must be true if the heat of polymerization is positive, the same rate of reaction (i.e., one which is in the observation time scale) would result by simultaneously increasing pressure and decreasing temperature—thereby providing the observed negative slope for the reaction boundary curve.

Chan and Jonscher[47] have reported that the high-pressure polymerization of CS_2 results in either poly(carbon disulfide) or a mixture of sulfur and semiconducting carbonaceous material of largely unknown nature. Since the reaction conditions used to obtain either of these materials are similar to those used by Butcher et al.[35] in their heat of formation measurements on poly(carbon disulfide), one could worry about whether or not the exothermic heat of polymerization obtained by Butcher et al.[35] is a result of degradation during the synthesis of poly(carbon disulfide) to form free sulfur and the semiconductor. However, this does not appear to be the case, since each high-pressure synthesis reaction used in the preparation of polymer for calorimetry was examined by infrared spectroscopy for the presence of the C=S bond at 1063 cm^{-1}.[35] Chan et al.[47] found that the partially degraded product (containing free sulfur and the semiconductor) showed a uniformly high absorption which masked all features of the infrared spectra.

Tsukamoto and Takahashi[29] have reported that carbon disulfide can be polymerized by using an anionic catalyst at ambient pressure and 10 °C. However, although there is evidence for C=S in the polymerization product, X-ray photoelectron spectroscopy indicates a 60% lower concentration of this functionality than is expected for either structure I or structure II poly(carbon disulfide). Also, Wall and Brown[48] have reported the γ-ray polymerization of CS_2 from ambient pressure and 62 °C to pressures up to 15 kbar and higher temperatures. The yield of polymers was low in all cases (about 4% and less). The product was not characterized, so it is difficult to draw many conclusions from this work. However, the product obtained at 62 °C and low pressures was tan colored and, therefore, does not appear to be either structure I or structure II poly(carbon disulfide). On the other hand, the product obtained by irradiation at high pressures is deep black and could correspond to one of these polymers.

Note that a variety of carbon diselenide polymers could be proposed that have 1:1 molar ratio of —Se— and C=Se groups. Specifically, the general class of polymers having CSe_2 stoichiometry and containing only —CSe—CSe— chain segments and selenium chain segments would provide the same agreement with the EXAFS data as does

structure II poly(carbon diselenide). The most attractive model for poly(carbon diselenide) is structure II only because this structure differs from the above alternate structures in not requiring complete disruption of covalent bonds present in the CSe_2 molecule. Based on results for model compounds, the above alternate structures containing variable numbers of seleniums in the selenium chain segments would appear to have lower free energy than does structure II. For example, dibenzyl diselenide is stable for at least 90 min at 109 °C. However, high-temperature thermal exposure (150–170 °C) of molten dibenzyl diselenide rapidly results in a mixture of dibenzyl polyselenides, $H_5C_6CH_2$–$(Se)_n$–$CH_2C_6H_5$, and free selenium.[49] Ignoring the amount of free selenium, which was not determined, the molar fractions of the degradation products (melt phase) were 50% for $n = 1$, 34% for $n = 2$, and 16% for $n > 2$. In contrast with these results, heating diphenyl diselenide up to 208 °C did not produce any evidence of degradation.[50] It has also been reported[51] that the diselenide ($n = 2$) of R_2NCSe–$(Se)_n$–$CSeNR_2$, where R is an alkyl group, disproportionates at low temperatures in a catalyzed solution to form a mixture of the monoselenide ($n = 1$) and the triselenide ($n = 3$). These results suggest, for example, that the structure $((Se)_3CSeCSeSeCSeCSe)_n$ would have lower free energy than does structure II poly(carbon diselenide).

Note that organic diselenides are typically thermochromic,[50] which is a consequence of the temperature-dependent width of the –SeSe– optical absorption band. Kuder and Lardon[50] have argued, via the Franck–Condon principle, that this thermochromism arises from the absorption of the –SeSe– band on the edge of the visible and the low frequency of the –SeSe– stretching vibration (about 260 cm^{-1}). Because of this low frequency, the population of vibrational energy levels for this chromophore is very dependent on temperature, which leads to the thermal broadening. Since we assign a similarly low Raman vibration frequency (244 cm^{-1}) to the Se–Se stretch in poly(carbon diselenide), it will be interesting to see whether any analogous thermochromism arises for poly(carbon diselenide).

Registry No. H_3COOCH_3, 690-02-8; H_3COCH_3, 115-10-6; H_3CCH_3, 74-84-0; $H_5C_2OOC_2H_5$, 628-37-5; $H_5C_2OC_2H_5$, 60-29-7; $H_5C_2C_2H_5$, 106-97-8; $C_6H_5SSC_6H_5$, 882-33-7; $C_6H_5SC_6H_5$, 139-66-2; $C_6H_5C_6H_5$, 92-52-4; H_3CSSCH_3, 624-92-0; H_3CSCH_3, 75-18-3; $H_5C_2SSC_2H_5$, 110-81-6; $H_5C_2SC_2H_5$, 352-93-2; $H_7C_3SSC_3H_7$, 629-19-6; $H_7C_3SC_3H_7$, 111-47-7; $H_7C_3C_3H_7$, 110-54-3; $H_9C_4SSC_4H_9$, 629-45-8; $H_9C_4SC_4H_9$, 544-40-1; $H_9C_4C_4H_9$, 111-65-9; $C_6H_5SeSeC_6H_5$, 1666-13-3; $C_6H_5SeC_6H_5$, 1132-39-4; poly(carbon dioxide), 114132-42-2; poly(carbon disulfide), 25948-29-2; poly(carbon diselenide), 82490-00-4.

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