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Bond Energy Scheme for Estimating Heats of Formation of Monomers and Polymers. VI. Sulfur Compounds

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ABSTRACT

The bond energy scheme is extended to sulfur compounds and heats of formation and atomization energy terms derived from thermochemical data reviewed to 1977, for bonds of sulfur with carbon, hydrogen, halogens, and oxygen atoms. A precision of ± 1 kcal/mole was attainable for the covalent bonds of divalent sulfur in the lowest oxidation state $S(\pm II)$. The higher valency states: $S(IV)$ and $S(VI)$ involve polar contributions depending upon the electronegativity of the combining atom as well as ($d^{\pi} - p^{\pi}$) orbital promotion energies which are specific to the compound and transferable to other molecules only with a limited precision, no better than about ± 3 kcal/mole. The atomization energy terms ($E_a^{25^{\circ}C}$) of various bonds of sulfur are found consistent with the experimental bond dissociation energies and bear a relationship with bond lengths and force constants as observed in the previous work. Heats of polymer-forming reactions and heats of formation of sulfur-containing monomers and polymers are estimated from the newly derived bond energy terms.

INTRODUCTION

In continuation of the earlier work [1-5] on energies of bonds of C, H, F, Cl, Br, I, and O atoms, the experimental data on heats of formation of sulfur compounds have been reviewed (to 1977), analyzed, and resolved in terms of bond energies for various sulfur bonds which are given in Table 1. The bond energy terms are compared with the experimental bond dissociation energies and a reasonable harmony between the two was observed. The energy terms are also consistent with bond lengths and force constants as envisaged in the Sutherland-Fox-Martin relationship extended by Somayajulu [27]. Strain energies for ring compounds, falling somewhat outside the scope of the additivity principle, have been listed as such in Table 1. A very recent extensive review of sulfur containing molecules and radicals by Benson [7] provided many good estimates of heats of formation and dissociation energies for sulfur compounds yet unstudied by direct calorimetry. Since the previous compilations of Stull, Westrum, and Sinke [9] and Cox and Pilcher [6] not much combustion calorimetric work was found in literature. These references have been the main source of experimental data for working out the bond energy terms in this work. ICSU-CODATA [18] and McBride's tables of thermodynamic properties to 6000°K [10] have been taken as the standard data on atoms and diatomic species shown in Table 2. Heats of formation of sulfur-containing polymers and heats of polymer-forming reactions based on the newly derived bond energy terms are dealt with in the last section.

Corrections to certain energy terms in the previous work are necessary in Table 2 of the previous paper [5] and other related tables. Term 2, namely C_2^3-O is revised as $\Delta H_f^0(g)$: -14.7 and $E_a = 87.3$ kcal/mole, in view of new thermochemical data of Fenwick et al. [29]. This work also gives rise to a few new 1-3 steric-interaction terms as mentioned in the "note added in proof" of the previous paper [5]. The term 48 i. e., (OC)O-O(CO) is revised in the light of recent precise calorimetric work on dibenzoyl peroxide [30]. The revised values are: $\Delta H_f^0(g) = +27.6$ and $E_a = 32.0$ kcal/mole. Terms 19, 20 and 50 in the same table are wrong due to obvious oversight. The correct terms are $C_0^2=O$, carbon dioxide: $-\Delta H_f^0(g) = -47.0$ and $E_a = 192.2$ kcal/mole; C^1-O , carbon monoxide = $-\Delta H_f^0(g) = -26.4$ and $E_a = 257.3$ kcal/mole; $O_2 = 0$, oxygen (gas, reference state): $E_a = 119.1$ kcal/mole.

TABLE 1. Bond Energy Terms and Ring Strain Energies for Calculating the Standard Heat of Formation/Atomization Energy (g, 25°C) of Sulfur Compounds

No.	Bond ^a	$\Delta H_f^0(g)$ $\pm \sigma$ (kcal/mole) ^b	Bond energy E_a 25°C (kcal/mole)	Bond dissociation energy (exptl.) ^c (kcal/mole)	Type (and no.) of compounds correlated	Reference
Divalent Sulfur Atoms: -S-						
Sulfur-hydrogen bonds						
1.	(C)S-H	-1.3 ± 0.4	86.5	88	Thiols (24)	[6]
2.	(S)S-H	0.0 ± 0.5	85.2		Sulfanes H ₂ S _x	[7, 8]
3.	S-H''	-2.4	87.6	92	H ₂ S	[9, 10]
Sulfur-carbon bonds						
4.	S-C ₃ ³	6.1 ± 0.5	69.8	73	Thiaalkanes (7)	[6]
5.	S-C ₂ ³	5.3 ± 0.5	70.6	71	Thiaalkanes (12)	[6]
6.	S-C ₁ ³	4.7 ± 0.4	71.2	70	Thiaalkanes (3)	[6]
7.	S-C ₀ ³	5.1 ± 0.6	70.8		Thiaalkanes (4)	[6]
8.	S''-C ₂ ³	5.0	71.0		Dithiaalkanes	[11]
9.	S-C ² (O)	3.8 ± 1.2	72.2		Thiol esters: (short bond) (6)	[6]
10.	S-C ² (S)	6.5 ± 2.5	69.4		Trithiocarbonate	[12]

(continued)

TABLE 1 (continued)

No.	Bond ^a	$\Delta H_f^\circ(g)$ $\pm \sigma$ (kcal/mole) ^b	Bond energy E_a (kcal/mole)	Bond dissociation energy (exptl.) ^c (kcal/mole) ^c	Type (and no.) of compounds correlated	Reference
11.	S-C ^{ϕ} , S-C ²	1.2 \pm 0.8	74.7	77	Thiaalkanes (4)	[6]
12.	S ^d -(C ^{π}) ¹	-8.8	84.8	89	Thiophene	[6]
13.	S-C ¹ (N)	-13.2	89.1	97	Dithiocyanogen	[6]
14.	S=C ² (H) ^d	27.6	124.3	124	S=CH ₂	[7]
15.	S=C ^{0e}	14.0	137.8	103	CS ₂ , COS	[6, 7]
16.	S ^{::::} C	70.0	167.5	174	CS	[7, 13]
Sulfur-sulfur bonds						
17.	(S)S-S(S)	3.44	62.7		Polymeric sulfur	[14, 15]
18.	(C)S-S(C)	2.3 \pm 0.5	63.9	68	Dithiaalkanes (5)	[6]
19.	S=S	30.7	101.7	103	S ₂	[16]
Sulfur-oxygen bonds						
20.	S-O ¹	-7.1	70.0		S(OH) ₂	[7]
21.	S=O	1.3	124.5	125	SO	[10]
Sulfur-halogen bonds						
22.	S-F ¹	-35.7	87.7	92	SF ₂	[13]
23.	(S)S-F	-41.7	93.7		S ₂ F ₂	[7]

24.	S-Cl ^{II}	-2.4	64.5	70	SCl ₂	[7, 10]
25.	(S)S-Cl	-4.0	66.1		S ₂ Cl ₂	[7, 10]
26.	(S)S-Br	2.8	57.0	62	S ₂ Br ₂	[7]
27.	S-I	(10)	(48)		Speculation	[17]
Tetravalent Sulfur Atoms: S ⁴						
28.	(O)S ⁴ -H ^{II}	9.8 ^f	58.9 ^f	63	O=SH ₂	[7]
28a	(S)S ⁴ -H ^{II}	-3.9 ^f	72.5 ^f	64	S=SH ₂	[7]
29.	S ⁴ -C ³	8.0 ± 1.0	51.4	50	Sulfoxides (4)	[6]
30.	S ⁴ -C ^φ , S ⁴ -C ²	4.0 ± 1.0	55.4	57	Sulfoxides (2)	[6]
31.	S ⁴ -O(C)	-18.0 ± 2.0	64.3	76	Sulfite esters (short bond)	[6]
32.	S ⁴ -O(H)	-19.4	65.7		H ₂ SO ₃	[7]
33.	(O)S ⁴ =C ²	26.6	92.1		CH ₂ =SO	[7]
34.	(O)S ⁴ =S	25.5	73.8	77	S ₂ O	[7]
35.	(C)S ⁴ =S (H)S ⁴ =S	8.9	90.4 ^f	53 (?)	S=S(Me) ₂ ; S=SH ₂	[7]
36.	S ⁴ -S ⁴	20.8	12.2 ^f	15	φSO-SOφ	[7]
37.	S ⁴ -S	11.1	38.6 ^f	36	φSO-Sφ	[7]
38.	S ⁴ ≧O ^{II}	-35.5	128.2	132	SO ₂	[10, 18]
39.	S ⁴ -F	-46.0	81.4	87	SOF ₂	[7, 19]
40.	S ⁴ -Cl	-7.5	53.0	58	SOCl ₂	[9]

(continued)

TABLE 1 (continued)

No.	Bond ^a	$\Delta H_f^0(g)$ $\pm \sigma$ (kcal/mole) ^b	Bond energy E_a 25°C (kcal/mole)	Bond dissociation energy (exptl.) ^c (kcal/mole) ^c	Type (and no.) of compounds correlated	Reference
41.	S ⁴ -Br	3.0	40.3	40	SOBr ₂	[7, 19, 20]
Hexavalent Sulfur Atoms: S ⁶						
42.	(O)S ⁶ -H ¹¹	-0.5	63.6		SO ₂ H ₂	[7]
43.	S ⁶ -C ³	-4.4 ± 1.5	58.3	62	Sulfones (15)	[6]
44.	S ⁶ -C ²	-6.7 ± 2.3	60.6	64	Sulfones (7)	[6]
45.	S ⁶ -C ^ϕ	-9.3 ± 1.8	63.2	73	Sulfones (9)	[6]
46.	S ⁶ -C ¹	-12.1 ± 2.0	66.0		Sulfones (2)	[6]
47.	S ⁶ -S	-4.1	48.2 ^f	42	ϕSO ₂ -Sϕ	[7]
48.	S ⁶ -S ⁴	-1.4	29.0 ^f	28	ϕSO ₂ -SOϕ	[7]
49.	S ⁶ -S ⁶	-23.6	45.7 ^f	41	ϕSO ₂ -SO ₂ ϕ	[7]
50.	S ⁶ -O(C)	-28.3 ± 1.1	69.1		Sulfate esters (4) (short bond)	[6]
51.	S ⁶ -O(H)	-30.6	71.4	88	H ₂ SO ₄ (g)	[7]
52.	S ⁶ -O(S ⁶)	-20.8	61.6		SO ₃ trimer	[7]
53.	S ⁶ =C ²	-2.4	110.1		CH ₂ =SO ₂	[7]
54.	S ⁶ =O ¹¹¹	-31.5	113.1	83	SO ₃	[6, 7]

55.	S^6-F	-48.6	78.5	88	SF_6	[7]
56.	$(O)S^6-F$	-58.2	88.1	88	SO_2F_2	[9, 21]
57.	$(O)S^6-Cl$	-11.2	51.2	63	SO_2Cl_2	[7]
58.	$(S^6)O-O(H)$	+25 ± 2	34.5 ± 2		H_2SO_5	[7, 22]
59.	$(S^6)O-O(S^6)$	+29 ± 2	30.4 ± 2		$H_2S_2O_8$	[7, 22]
60.	$(S)C^2-H''$	-1.8	96.7		$O=CH_2$	[5]
61.	$(O)S^6=S$	21.4	66.9		$H_2S_2O_3^G$	[23, 24]

Ring-Strain Corrections

Thiacyclanes



+19.4



+19.2



+1.2



+3.2



+5.0



0.0

[6]

[6]

[6]

[6]

[6]

[6]

(continued)

TABLE I.(continued)

No.	Bond ^a	$\Delta H_f^0(g)$ $\pm \sigma$ (kcal/mole) ^b	Bond energy E_a (kcal/mole)	Bond dissociation energy (exptl.) (kcal/mole) ^c	Type (and no.) of compounds correlated	Reference
	Cyclo-S ₇	+3.7				[6]
	Larger rings					
		Unpredictable				
	Elemental sulfur rings					
	C-S ₃	+22.2				[7, 23]
	C-S ₄	+17.2				[7, 23]
	C-S ₅	(+8)				[7, 23]
	C-S ₆	+3.9				[7, 23]
	C-S ₈	-3.2 ^h				[7, 23]
	-S _x -(open chain)	0.0 ^h				[7, 23]

^a Atoms shown in parenthesis are associated with the bonding atom.

^b Standard deviation of the mean; for the number of compounds correlated (penultimate column).

^c Bond dissociation energies are taken mostly from Benson [7] and Mackle [25]; others are from Kerr [26].

- d Thiocarbonyl bond, recommended for thio-(aldehydes and ketones).
- e Thiocarboxyl bond, recommended for thio-(acids, acid-halides and carbonates).
- f These energy terms are rather speculative, based on Benson [7], but with an assumption that the bond strengths of $S^4=O$ and $S^6=O$ are virtually constant and transferable; see text.
- Independently calculated from Monger and Redlich [22], assuming $\Delta S_R = 9$ e. u. as the mean of experimental ΔS and the a priori estimate of Benson. The O-O bond energy terms come close to those for dibenzoyl peroxide and peroxy carbonate [5].
- g Determined from $\Delta H_f^0(\text{aq})$ of sodium thiosulfate [24].
- h Ring strain estimated with respect to open chain, $-S_x^-$; S_8 ring is more stable than the polymer $-S_x^-$ by 3.17 kcal/mole as shown by Tobolsky [15].

TABLE 2. Heats of Formation of Atoms and Key Compounds

Species	ΔH_f^0 (g) (kcal/mole)	Reference
H	52.10	[18]
C	171.29	[18]
F	18.86	[6, 10]
Cl	28.99	[18]
Br	26.73	[18]
I	25.52	[18]
O	59.55	[18]
S	66.2	[6, 7, 10, 18]
S ₂	30.7	[18]
CS	70.0	[16]
OCS	33.0	[9]
CS ₂	28.0	[9]
SO	1.31	[10]
SO ₂	-70.94	[18]
SO ₃	-94.5	[7, 10]
H ₂ S	-4.82	[10]
H ₂ S ₂	3.8	[7, 23]
SF ₂	-71.4	[13]
S ₂ F ₂	-80.0	[7]
SF ₄	-183 ± 5	[7]
SF ₆	-291.6	[28]
SCL ₂	-4.8	[7]
S ₂ Cl ₂	-4.7	[7]
SBr ₂	5.0	[7]
SOF ₂	-130 ± 5	[7, 19]
SO ₂ F ₂	-179.3	[19, 21]
SOCl ₂	-50.5	[9]

TABLE 2. (cont.)

Species	$\Delta H_f^0(g)$ (kcal/mole)	Reference
SO ₂ Cl ₂	-85.4	[9]
SOBr ₂	-29.6	[9]
c-(SO ₃) ₃	-314.0	[7]

DERIVATION OF ENERGY TERMS

Divalent sulfur-carbon bonds, with primary, secondary, or tertiary hydrogens on the carbon atom, were derived from selected and accurate data on thiaalkanes [6]; these are shown as terms 4-7 and 10 and 11 in Table 1. Energy term 8 represents bond with methylene group sandwiched between two divalent sulfur atoms, which is stronger than the normal S-C₂³ bond as revealed in the special study of relevant dithiaalkanes [11]. This behavior is similar to the methylene group between two oxygen atoms as observed in the earlier work [5]. The sulfur-sulfur bond energy term 18 is derived from other dithiaalkanes [6]. The S-S bond appears to be weaker in elemental sulfur such as the S₈ ring [14] or in the open chain polymeric sulfur -S_x- [15] for which the energy term 17 is derived, recognizing that the heat of polymerization of S₈ → -S_x-, independently determined, is + 3.17 kcal/mole. Sulfur-oxygen single bond, term 20, and many other terms are based on the estimate of $\Delta H_f^0(g)$ for S(OH)₂ given by Benson [7]. The bond in SO [31, 32] appears to be a covalent double bond with strength comparable to C=C. The sulfur-halogen bonds are represented by energy terms 22-27. The S-I bond is speculative [17], since no chemical compound with sulfur-iodine bond is yet known.

The tetravalent sulfur-oxygen bond, S⁴=O, is taken from the well established value of $\Delta H_f^0(SO_2, g)$. Using this bond energy (term 38) for S⁴=O throughout, the other sulfur bonds in sulfoxides and sulfite esters, namely the energy terms 29 and 30 for S⁴-C and 31 for S⁴-O, the "short" bond of the sulfite esters, were resolved. The S⁴-halogen bonds (terms 39, 40, 41) were determined from relevant compounds as shown in Table 1.

Among hexavalent sulfur bonds, the three equivalent hybridized bonds in sulfur trioxide molecule (term 54) were taken as the basis for S⁶=O in sulfones, sulfate esters, and sulfonyl halides and other

bonds determined from the simple additivity rule. These are given as energy terms 42 through 59 in Table 1. Special energy terms were necessary to account for the heat of formation/atomization of the following molecules: energy terms 32 and 51 for $\text{H}_2\text{SO}_3(\text{g})$ and $\text{H}_2\text{SO}_4(\text{g})$, respectively, and term 56 for SO_2F_2 . Energy term 13 ($\text{S}-\text{C}^1$) is obtained from dithiocyanogen assuming that $\Delta H_f(\text{C}-\text{N}) = +53.2$ kcal/mole taken from as yet unpublished work on nitrogen compounds. The last energy term, of Table 1, namely $(\text{S})\text{C}^2-\text{H}''$, the carbon-hydrogen bond when the sp^2 carbon is bonded to an electronegative atom or group such as, $=\text{S}$, $=\text{SO}$, $=\text{SO}_2$ etc., is assumed to be the same as in formaldehyde, namely $\Delta H_f^0(\text{g}): |(\text{O})\text{C}^2-\text{H}''| = -1.8$ kcal/mole or $E_a = 96.7$ kcal/mole determined in earlier work [5].

RING STRAIN

Strain energies of three- and four-membered thiacycloalkanes (one sulfur atom) are considerably reduced, by about 7-8 kcal, due to the substitution of larger sulfur atom into corresponding cycloalkanes. Such lowering of strain due to oxygen atom substitution was earlier found to be only about 1 kcal, and only for the first oxygen atom introduced [5]. The ring strain is nearly the same for either three- or four-membered rings containing one heteroatom, and is sizable, being 19 kcal/mole for thiacycloalkanes. More sulfur atoms in the ring seem to increase or decrease the strain, depending upon the size of the ring, as seen from the ring-strain of elemental sulfur rings. Among five-membered thiacycloalkanes, the basic ring strain is only about 1.2 kcal in thiacyclopentane and its methyl derivatives. It is found to increase by about 1 kcal per sp^2 carbon introduced in the ring, as judged from the experimental $\Delta H_f^0(\text{g})$ values for 2- and 3-thiacyclopentenes [33]. Our estimate of ring strain in thiophene with 4 sp^2 carbons is about 5 kcal/mole. These and estimates of strain energies in elemental sulfur rings are shown at the end of Table 1.

DISCUSSION

The thermochemical data on divalent sulfur compounds are fairly well established and self-consistent [6, 7, 9], allowing the empirical methodology of additivity of bond energies, to be successful within ± 1 kcal/mole uncertainty shown against the energy terms in Table 1. For tetravalent and hexavalent sulfur, ample data exist on sulfoxides and sulfones. The calculated heats of formation and atomization

energies of these compounds, using the recommended terms agree with the experimental data within ± 2 kcal/mole for S^4 and S^6 compounds. A comparison of calculated and observed values has not been exercised in this work since very little new work has appeared on sulfur thermochemistry after the previous excellent reviews [6, 9].

Somayajulu's extension [27] of the Sutherland-Fox-Martin (S-SFM) correlation, namely the substitution of bond-energy for bond-dissociation energy, works fairly well for various types of sulfur bonds identified in this work, giving rise to a unique mean value of $\bar{S}_{ij} = 0.168 \pm 0.03$ (a dimensionless quantity in conventional units) (Table 3). If the units for the variables, r , k , and E_a are converted to absolute cgs-units the value of Somayajulu-(SFM) constant for all chemical bonds so far encountered in this series comes to: $\bar{S}_{ij} = 14.7 \pm 2.6$

arbitrary units = 21.16 ± 3.74 , an absolute number in cgs units. The significance of this observation is not understood at present; but it seems possible that some exact function of these variables, which should also include electronegativity factor [79] besides r , k , E and μ , may be evolved in future to hold universally for any chemical bond. The S_{ij} constants for various chemical bonds are given in Table 4.

It may be seen from Table 4 that the constancy of S_{ij} is fairly good for C, O, and S bonds but the scatter in S_{ij} for bonds of hydrogen atom and for homonuclear bonds is large, namely ± 8 . A tentative modification of the S_{ij} function to $S_{ij}/\mu^{1/2}$ imparts some convergence to the constancy, viz., the overall $S_{ij}/\mu^{1/2} = (5.7 \pm 2) \times 10^{-2}$ for all 34 bonds despite the 'constant' for hydrogen atom varying from 4 to 11.

The energies of sulfur bonds (E_a^{25}) identified in Table 1 are found to be very consistent with the bond dissociation energies (mostly experimental) shown. In the development of the previous bond-energy scheme [1-5] and its present extension to sulfur compounds, certain energy terms which are derived from "key" compounds have to be assumed as the basic parameters, at least one per new element, per valency state, introduced in the scheme. Our choice for E_a of the S=O bond in tetravalent sulfur, had been one of the two bonds of SO_2 (128.2 kcal) and for S=O in hexavalent sulfur, one of the three equivalent hybridized bonds of SO_3 (113.1 kcal). The resulting bond strength E_a for the S^4 -C bond in sulfoxides works out to about 51 kcal, some 10 kcal lower than S^6 -C in sulfones, in full accord with the corresponding experimental dissociation energies of these bonds [25], and justifying the choice of these key compounds. The divalent sulfur S-C bond in thiaalkanes is considerably stronger, namely 70 kcal. The strongest

TABLE 3. Fundamental Properties of Sulfur Bonds Identified in the Bond Energy Scheme and Their Correlation

Bond	E_a 25°C (kcal/mole)	Bond length r_a (Å)	Force constant k (mdyne/Å)	ν str (cm^{-1}) ^a	S-SFM constant ($S_{ij} = kr^2/E$) $\times 10^2$	Source Compound	Reference
Sulfur-hydrogen bonds: ($\bar{S}_{ij} = 8.0 \pm 0.4$)							
(C) S-H	86.5	1.329	3.80	2573	7.76	MeSH	[34, 35]
S-H''	87.6	1.335	4.14	2632	8.42	H ₂ S	[36]
(S) S-H	85.2	1.35	3.69	2509	7.89	H ₂ S ₂	[36, 37]
Sulfur-carbon bonds: ($\bar{S}_{ij} = 14.8 \pm 3.1$)							
S-C ³	69.8	1.816	3.21	742	15.17	(Me) ₂ S	[34]
S ⁴ -C ³	51.4	1.84	3.187 ^b	611	20.99	DMSO	[38]
S ⁶ -C ³	58.3	1.90	3.03 ^b	770	18.76	(Me) ₂ SO ₂	[39]
S-C ² (O)	72.2	2.00	2.20	625	12.18	Thiol esters	[40, 78]
S ^d -C ⁷	84.8	1.714	4.794	839	16.60	Thiophene	[41]
S-C ¹	89.1	1.701	4.08	690	13.25	S ₂ (CN) ₂	[42]
S=C ² (H)	124.3	1.71	5.84	1150	13.74	S=CH ₂	[7, 43, 44]
S=C ² (S)	69.4	1.65	3.1	1062	12.16	Trithiocarbonate	[12, 43]
(S)''=C ⁰	137.8	1.553	7.5	1523	13.13	CS ₂	[45, 46]
S ^{.....} C	167.5	1.535	8.4	1282	11.82	CS	[45, 46]

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Sulfur-sulfur bonds: ($\bar{S}_{ij} = 16.3 \pm 3.8$)					
(S)S-S(S)	62.8	2.048	1.85 ^b	475	12.36
S=S	101.7	1.889	5.0	725	17.54
S ⁴ =S	73.4	1.884	4.43	672	21.42
S ⁴ -S ⁶	29.0	2.39	(0.8) ^c	(292) ^c	(16)
S ⁶ -S ⁶	45.6	2.25	(1.6) ^c	(413) ^c	(16)
Sulfur-oxygen bonds: ($\bar{S}_{ij} = 16.3 \pm 2.1$)					
S-O	70.0	(1.7) ^c	(3.88) ^c	(788) ^c	(16)
S ⁴ -O	64.3	(1.7) ^c	3.28	725	14.74
S ⁶ -O	69.1	1.60	4.37	796	16.19
S=O	124.5	1.481	7.94	1251	13.99
S ⁴ ⇒O	128.2	1.432	9.97	1151	15.95
S ⁶ ⇒O	113.1	1.418	10.75	1070	19.11
Sulfur-fluorine bonds: ($\bar{S}_{ij} = 16.2 \pm 1.0$)					
S-F	87.7	1.592	5.30	840	15.32
S ⁴ -F	81.7	1.585	5.4	808	16.40
S ⁶ -F	78.5	1.564	5.45	775	16.98
Sulfur-chlorine bonds: ($\bar{S}_{ij} = 17.6 \pm 3.2$)					
S-Cl	66.1	2.01	2.28 ^b	457	13.93

(continued)

TABLE 3 (continued)

Bond	E_a 25°C (kcal/mole)	Bond length r_a (Å)	Force constant k (mdyne/Å) ^a	ν_{str} (cm ⁻¹) ^a	S-SFM constant ($S_{ij} = kr^2/E$) $\times 10^2$	Source compound	Reference
S ⁴ -Cl	53.0	2.07	2.36	455	19.08	SOCl ₂	[36, 58]
S ⁶ -Cl	51.2	2.01	2.52	400	19.88	SO ₂ Cl ₂	[50, 52]
Sulfur-bromine bonds: ($\bar{S}_{ij} = 20.7 \pm 0.3$)							
S-Br	56.6	2.24	2.36	355	20.92	S ₂ Br ₂	[17, 59]
S ⁴ -Br	40.3	2.27	1.6	379	20.45	SOBr ₂	[19, 20]

^aUnless covered by specific reference in the last column, the force constant and stretch frequency are taken from Herzberg [46] and Evans and Wagman [60]. Where force constant is not available from normal coordinate analysis by the spectroscopist, the same is calculated from the well known approximation of Bentley et al. [61]. $\nu_{str} = 1307 (k/\mu)^{1/2}$ where ν_{str} is asymmetric stretch frequency, μ is the reduced atomic mass = $m_1 m_2 / (m_1 + m_2)$, and k is the required force constant in (dynes/cm) $\times 10^5$.

^bThe value is inconsistent and suggests that the force constant for this bond, assumed initially in the normal coordinate analysis, perhaps needs a revision.

^cPredicted (calculated) value shown in parenthesis.

TABLE 4. Somayajulu-(SFM) Constants for Chemical Bonds

Bond	$S_{ij} \times 10^2$	Reduced mass, μ (atomic)	$S_{ij}/\mu^{1/2} \times 10^2$
Carbon			
C-C	11.8 ± 1.0	6.00	4.82
C-H	(5.9 ± 0.2) ^a	0.92	4.24
C-F	11.0 ± 1.0	7.35	4.06
C-Cl	13.1 ± 0.9	8.97	4.37
C-Br	16.3 ± 1.5	10.43	5.05
C-I	(20 ± 5) ^{a,b}	10.96	6.04
C-O	11.0 ± 0.7	6.86	4.20
C-S	<u>14.8 ± 3.0</u>	8.73	<u>5.00</u>
Avg.	13.0 ± 2.2		4.7 ± 0.7
Oxygen			
O-O	14.4 (O ₂) ^c	8.00	5.09
O-H	(6.6 ± 0.7) ^a	0.94	6.80
O-C	11.0 ± 0.7	6.86	4.20
O-S	<u>16.0 ± 2.1</u>	10.67	<u>4.90</u>
Avg.	13.8 ± 2.6		5.3 ± 1.1
Sulfur			
S-S	16.3 ± 3.8	16.0	4.08
S-H	(8.0 ± 0.4) ^a	0.97	(8.12)
S-C	14.8 ± 3.0	8.73	5.00
S-F	16.2 ± 1.0	11.92	4.63
S-Cl	17.6 ± 3.2	16.83	4.31
S-Br	20.7 ± 0.3	22.85	4.33
S-O	<u>16.0 ± 2.1</u>	10.67	<u>4.90</u>
Avg.	16.9 ± 2.0		4.5 ± 0.4
Overall average for C, O, and S bonds:	14.7 ± 2.6		5.0 ± 1.1

(continued)

TABLE 4. (cont.)

Bond	$S_{ij} \times 10^2$	Reduced mass, μ (atomic)	$S_{ij}/\mu^{1/2} \times 10^2$
Hydrogen			
H-H	3.0	0.50	4.24
H-C	5.9 ± 0.2	0.92	6.14
H-F	6.1	0.95	6.26
H-Cl	8.1	0.97	8.21
H-Br	9.4	0.99	9.46
H-I	11.4	0.99	11.44
H-O	6.6 ± 0.7	0.94	6.80
H-S	8.0 ± 0.4	0.97	8.12
Avg.	7.3 ± 2.6		7.6 ± 2.3
Homonuclear bonds			
H-H	3.0	0.50	4.24
C-C	11.8	6.00	4.82
F-F	24.2	9.5	7.85
Cl-Cl	22.5	17.8	5.33
Br-Br	24.4	39.5	3.88
I-I	23.7	63.4	2.97
O-O	27.7 ^d	8.0	9.80
S-S	16.3	16.0	4.08
Avg.	19.2 ± 8.3		5.37 ± 2.3
Overall average for $S_{ij}/\mu^{1/2}$ for all bonds			
			5.8 ± 2 (34)

^a Excluded from average.

^b Bonds of iodine do not fit in.

^c Bonds of peroxide linkages do not fit in; oxygen molecule, O₂ is taken.

^d Peroxide O-O; revised (see text).

C-S bond (89 kcal) is formed with the acetylenic carbon atom sp^1 , while its normal value in other compounds is around 50-70 kcal. The S^d-C^π single bond in thiophene is also stronger than the normal C-S, by about 10 kcal, assuming that the ring-strain in thiophene is 5 kcal/mole. The "resonance" energy of thiophene, equivalent to two such excess bond energies, is thus about 20 kcal/mole, attributable to $d^\pi - p^\pi$ orbital overlap. This delocalization effect seems to be pronounced only in the monocyclic thia aromatic and is not associated with the mere bridging of two aromatic moieties by divalent sulfur. Thus in thianthrene, the calculated ($\Delta H_f^0(g)$) using the normal C^2-S bond comes to 71.6 kcal/mole; hence the stabilizing resonance energy is negligible, since the six-membered thianthrene ring may be only slightly strained. The experimental heat of formation of thianthrene (c) is 44.03 ± 0.36 kcal/mole [62] and its heat of sublimation, about 27 ± 2 kcal/mole estimated by Bondi's procedure [63, 64] which gives $\Delta H_f^0(g) = 71$ kcal/mole. The resonance energy of 16.8 kcal/mole for thianthrene calculated by Mortimer [65] does not seem to be in order.

The double bond between divalent sulfur and carbon is analogous to the carbon-oxygen double bond; namely: ketone ($C=O$: 167.5) while thioketone ($C=S$: 114.7 kcal); carboxylic acid ($C=O$: 178.5 kcal) while thiocarboxylic acid ($C=S$: 137.8 kcal). The "short" bond in carboxylic ester (C^2-O : 101.4 kcal) may be compared with C^2-S : 72.2 kcal in thiol esters. The bonds of sulfur and oxygen show an energy pattern similar to the bonds of carbon and oxygen, for example: energies of $S=O$, in SO (124.5 kcal) and in SO_2 (128.2 kcal), may be compared to the ketonic CO (167.5 kcal) and in CO_2 (192.2 kcal). The energy of $S=O$ (113.1 kcal) in SO_3 is comparable to $C=O$ (181.6 kcal) in ketene.

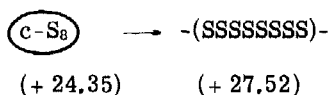
The S-S bond in dithiaalkanes, sulfanes or polysulfides is about 63 kcal in energy, some 30 kcal stronger than O-O in peroxides. Sulfur thus provides adequately strong covalent crosslinkages in rubber vulcanization as well as in the main polymer chain of polysulfide rubbers. Single bonds of sulfur with other elements: carbon, oxygen, chlorine, are all in general weak, however, ranging around 60 ± 10 kcal. Compounds of sulfur are therefore chemically reactive and thermally unstable. This factor was significant in designing and looking for new sulfur containing polymer structures with good mechanical strength or thermal stability. Besides polysulfide rubber putties (S-S: 64 kcal) and aromatic polysulfones (S^p-C : 63 kcal), not many polymers of industrial utility have emerged in this otherwise fertile area of novel synthetic polymers. Sulfur-fluorine bonds are the only strong ones (80-90 kcal) such as with tetravalent and hexavalent sulfur, comparable to C-C: 85-135 kcal; C-H: 97-102

kcal; C-O: 85-180 kcal; and C-Cl: 85 kcal; C-F: 106-118 kcal; which essentially prevail on the entire domain of organic polymers. Accordingly, some fluoro-sulfur elastomers such as poly(thiocarbonyl fluoride) were developed and evaluated [66-68], but these failed due to thermal stability limitations set by the weakest C-S linkages in the elastomer. Another important sulfur-containing industrial elastomer is chlorosulfonated polyethylene (Hypalon), where $-\text{SO}_2\text{Cl}$ groups are anchored randomly to the backbone chain, to the extent of about a few percent. Here again, the C-S (58 kcal) link is the weakest, and only about 40% of the total sulfonyl chloride contents participate and serve in vulcanization, the remaining groups being lost by desulfonation at the vulcanization temperature of 140°C [69]. Other sulfur-containing polymers are relatively unimportant industrially but of immense academic interest in the area of biopolymers [70] to make thermodynamic assessments on various life processes.

Some classical routes leading to sulfur polymers, are selected mainly from Sorenson and Campbell [67] and heats of formation of reactants and the product-polymer, and the heat of polymerization worked out. The sulfur bonds encountered in these reactions are: S-S: 63.9 kcal; C-S: 70.6 kcal; $\text{S}^{\text{II}}-\text{Cl}$: 51.2 kcal; $\text{S}^{\text{IV}}-\text{F}$: 81.4 kcal; $\text{S}^{\text{VI}}=\text{O}$: 113.1 kcal; $\text{S}^{\text{IV}}=\text{O}$: 128.2 kcal, and the sulfonic ester "short" bond $\text{S}^{\text{VI}}-\text{O}(\text{C})$: 69.1 kcal, besides other energy terms taken from the previous work [1-5]. Figures in parentheses in the following reactions represent the heat of formation (gas phase, 25°C).

POLYMERIC REACTIONS

1. Elemental Sulfur [15]:



$$\Delta H_p^0(\text{gg}) = + 3.17 \text{ kcal/mole}$$

2. Polymerization through C=S and C=O Bonds

Table 5 gives the heats of formation of monomers and polymers and heats of polymerization through opening of C=S or C=O double bond. The calculated heats of formation of strain free polymer structures in hypotheticalal gas phase may be considered very reliable for conversion to the condensed phase by combining these with estimates of heat of vaporization and cohesive energies available in many

TABLE 5. Heats of Formation and Polymerization through C=O and C=S Double Bonds

System	Monomer ΔH_f^0 (g) (kcal/mole)	Polymer structure	Polymer ΔH_f^0 (g) (kcal/mole)	Heat of polymerization		Reference
				ΔH_p^0 (gg) (kcal/mole)	Strain energy ^a	
Formaldehyde	-25.9 ^b	$\begin{array}{c} \text{H} \\ \\ \text{-OC-} \\ \\ \text{H} \end{array}$	-39.4	-13.5	0.0	[5, 71]
Thioformaldehyde	24.0	$\begin{array}{c} \text{H} \\ \\ \text{-SC-} \\ \\ \text{H} \end{array}$	4.6	-19.4	0.0	
Acetaldehyde	-39.7 ^b	$\begin{array}{c} \text{H} \\ \\ \text{-OC-} \\ \\ \text{C} \end{array}$	-49.4	-9.7	+0.7	[5, 71]
Thioacetaldehyde	10.3	$\begin{array}{c} \text{H} \\ \\ \text{-SC-} \\ \\ \text{C} \end{array}$	-2.4	-12.7	0.0	

(continued)

TABLE 5 (continued)

System	Monomer ΔH_f^0 (g) (kcal/mole)	Polymer structure	Polymer ΔH_f^0 (g) (kcal/mole)	Heat of polymerization		Reference
				ΔH_p^0 (gg) (kcal/mole)	Strain energy ^a	
Acetone	-52.0 ^b	C	-56.0	-4.0	+9.4	[5, 71]
		-OC- C				
Thioacetone	-2.1	C	-9.8	-7.7	(0.0) ^c	[72, 80]
		-SC- C				
Phosgene	-52.5 ^b	Cl	-53.6	-1.1	(+5)	[5, 71]
		-OC- Cl				
Thiophosgene	-6.4	Cl	-7.4	-1.0		
		-SC- Cl				

Carbonyl fluoride	-152.9 ^b	-133.6	19.2	(+2)	[5]
Thiocarbonyl fluoride	-83.7	-87.6	-3.9	0.0	

^a Estimated strain energy in the polymer chain (condensed state) which must be taken into account along with the tabulated ΔH_p^0 (gg) to judge the actual heat of polymerization and polymerizability of the monomer; arbitrary estimates of strain energy are parenthesized.

^b Experimental value.

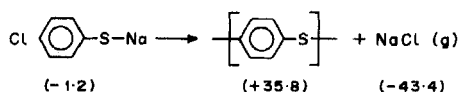
^c Whereas some strain was to be expected in this polymer, in analogy with polyisobutylene or polyacetone, the ready polymerizability of thioacetone and its ΔH_p^0 (1c) = -2.6 and ΔS_p^0 (1c) = -11.7 e. u. estimated by this author, through recalculation of the experimental, equilibrium polymerization data [72], indicate to the contrary [80].

group contribution schemes [71]. The strain in the polymer chain due to 1-3 interaction from the crowding $>C(CH_3)_2$ groups, appears to be negligibly small in polythioacetone in view of its good polymerizability in liquid and solid phases [72, 80].

It may be seen from Table 5 that polymerization of thioformaldehyde, thioacetaldehyde, and thioacetone are thermochemically much more facile than that of their corresponding oxygen analogs, especially the case of acetone. Carbonyl fluoride polymerization is precluded on account of much stronger C^2-F bonds in the monomer than C^3-F in the polymer. Thiocarbonyl fluoride, on the other hand, should readily polymerize at low temperatures [72], with its $\Delta H_p^0(\text{gg}, 25^\circ\text{C})$ of about 4 kcal/mole.

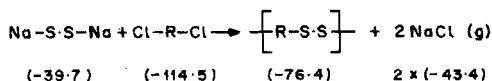
3. Polythioethers and polysulfides

Aromatic polythioethers: Lenz linear polymer [73]



$$\Delta H_p^0(\text{gg}) = -6.4 \text{ kcal/mole}$$

Aliphatic polysulfides; model reaction [74]

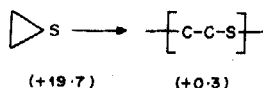


values for R = $(\text{CH}_2, \text{CH}_2\text{-O-CH}_2\text{-O-CH}_2\text{-CH}_2)$

$$\Delta H_p^0(\text{gg}) = -9.0 \text{ kcal/mole}$$

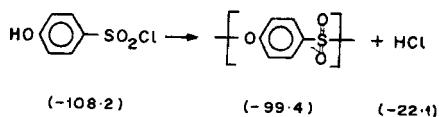
For aromatic polythioethers and aliphatic polysulfides, thermochemical data on NaS and NaCl have been taken from the JANAF tables [24] and the bond energies: $\Delta H_f^0(\text{g})$ for S-Na and Cl-Na bonds were estimated as -21.0 and -21.7 kcal/mole, respectively.

Ring opening of cyclic sulfides:



$\Delta H_p^0(\text{gg}) = -19.4 \text{ kcal/mole}$, essentially the ring strain energy.

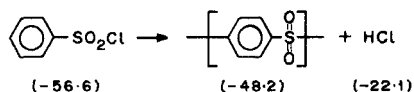
4. Polysulfonates [67]



$\Delta H_p^0(\text{gg}) = -13.1 \text{ kcal/mole}$

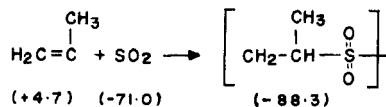
5. Polysulfones

Model reaction; aromatic polysulfones [75]



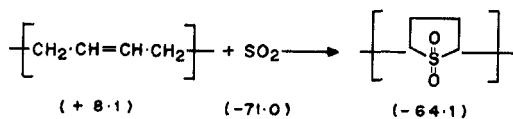
$\Delta H_p^0(\text{gg}) = -13.7 \text{ kcal/mole}$

Alkene-SO₂ copolymers [67]

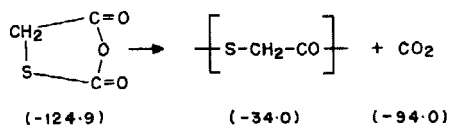


$\Delta H_p^0(\text{gg}) = -22.0 \text{ kcal/mole}$; exptl. value: -20.2 (sc) [76]

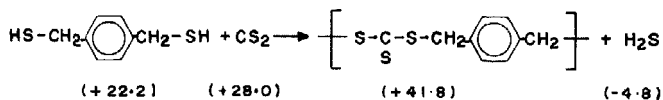
Polybutadiene-SO₂ cyclic sulfone [67]



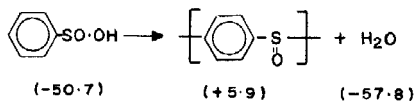
$\Delta H_p^0(\text{gg}) = -1.2 \text{ kcal/mole}$; less ring strain, if any.

6. Polythiol Esters [68]

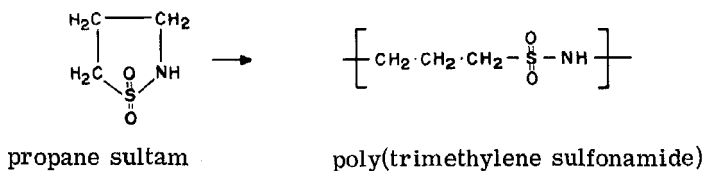
$\Delta H_p^0(\text{gg}) = -3.1$ kcal/mole; more negative perhaps by 2 kcal due to strain in the 5 membered $-\text{S}-\text{O}-$ ring.

7. Polythiocarbonates [68]

$\Delta H_p^0(\text{gg}) = -13.2$ kcal/mole

8. Polysulfoxides [68]

$\Delta H_p^0(\text{gg}) = -1.2$ kcal/mole

9. Polysulfonamides [68]

$-\Delta H_p^0(\text{gg}) = \text{Ring strain in sultam} (\approx 5 \text{ kcal/mole})$: S^6-N and $\text{N}-\text{H}$ remain unaltered on polymerization.

It may be seen that most of the above reactions leading to sulfur-containing polymers, are only mildly exothermic, ΔH_p^0 seldom exceeding 13 kcal/mole, except for the copolymerization of alkenes

+SO₂ where the heat of vinyl polymerization (20 kcal/mole) also contributes besides the heat of S⁴ → S⁶ promotion. In other reactions, elimination (formation) of HCl, NaCl, H₂O, H₂S, or ring strain provide the main driving force for the reaction.

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