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THE THERMOCHEMISTRY OF SULPHUR-CONTAINING MOLECULES AND RADICALS—III

THE THERMODYNAMIC PROPERTIES OF ORGANO-SULPHUR COMPOUNDS AND THE THERMODYNAMICS OF SOME OF THEIR REACTIONS

H. MACKLE and P. A. G. O'HARE

Dept. of Chemistry, David Keir Building, Queen's University, Belfast.

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IN PART I[1] of this series we listed the gas-phase heats of formation of (i) over one hundred organo-sulphur compounds; (ii) a number of inorganic sulphur-containing species of key importance. These data were used in Part II[2] to derive values for the dissociation energies of bonds involving sulphur and for the heats of formation of sulphur-containing free radicals. In the present paper we survey the literature dealing with the general thermodynamic properties of organo-sulphur compounds and discuss the thermodynamics of some of their more important reactions. An extensive compilation[3] of the thermodynamic properties of one hundred *linear* alkane thiols, sulphides and disulphides appeared some time ago. In Table 1 we list fifty additional sulphur-containing compounds for which thermodynamic data have become available during the past decade up to December 31st, 1962. The key to the letter symbols used in Table 1 is self-explanatory and as follows:

a. C_p of solid
b. C_p of liquid
c. C_p of gas
d. Transition temperature
e. Heat of transition
f. Triple (or melting) point
g. Fusion heat.
h. Vapour pressure of solid
i. Vapour pressure of liquid
j. Heat of sublimation
k. Heat of vaporisation
l. Entropy of solid, liquid
m. Entropy of gas
n. Data of state
p. $(G^\circ - H_0^\circ)$ or $(G_0 - H_0^\circ)/T$.
q. $(H^\circ - H_0^\circ)$ or $(H^\circ - H_0^\circ)/T$.

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TABLE 1

Compound	Property	Reference
Thiols		
1. 2-Methyl-1-propanethiol	a b c g i k l m n p q	4
2. 2-Propanethiol	a b c d e f g i k l m n p q	5
3. 2-Methyl-2-propanethiol	a b c d e f g i k l m n p q	6
4. 2-Butanethiol	a b c g i k l m n p q	7
5. 2-Methyl-2-butanethiol	a b c d e g i k l m n p q	8
6. 3-Methyl-1-butanethiol	a b c g i k l m	9
7. Benzenethiol	a b c f g i k l m n p q	10
Thia-alkanes		
8. 2,4-Dimethyl-3-thiapentane	a b c g i k l m	9, 11
9. 3-Methyl-2-thiabutane	a b c g i k l m n p q	11, 12, 13
10. 3,3-Dimethyl-2-thiabutane	a b c g i k l m p q	14
Thiacycloalkanes		
11. Thiacyclopropane	c i k m p q	15
12. Thiacyclobutane	a b c d e g i k l m p q	16
13. Thiacyclopentane	a b c g i k l m n p q	17
14. Thiacyclohexane	b c d g k l m n p q	18
15. Thiacycloheptane	f	19
16. Cyclopentanethiol	a b c g i k n p q	20
17. Cyclohexanethiol	a b c g i k l m	9
18. Cyclopentyl-1-thiaethane	a b d e g i k l m	9

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TABLE 1 (contd)

Compound	Property	Reference
Thiophenes		
19. Thiophene	a c h k m p q	21, 22
20. 2-Methylthiophene	a b c f g k l m n p q	23
21. 3-Methylthiophene	a b c f g k l m n p q	24, 25
22. Benzothiophene	a b c d e f g l	23
Miscellaneous		
32. Isothiocyanic acid	c m p q	26
24. Trifluoromethanethiol	a c d g h k	27
25. Methyl isothiocyanate	c m p q	28
26. Trimethyl sulphonyl methane	a l	29
27. Dimethyl sulphoxide	c m p q	30, 31, 32
28. Dimethyl sulphone	c m p q	30, 33
29. Thiolacetic acid	c m p q	28
30. β-Thiolactic acid	a b g l	34, 35
31. $\beta\beta'$-Dithiolactic acid	a l	34, 35
32. 2-Aminoethane sulphonic acid	a l	36
33. Ethyl sulphite	i k	37
34. Thiourea	c m p q	28
35. Cysteine	a l	34, 35, 51, 52
36. Cystine	a l	34, 35, 51, 52
37. Phenothiazine	i	53
38. 1,3,5,7 Tetramethyl-2,4,6,8 tetrathia-adamantane	c m p q	50

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TABLE 1 (contd)

Compound	Property	Reference
Inorganic		
39. S (rhombic)	a b c d e g h j l m n p q	38
40. S_8	c m p q	39, 40
41. CS_2	c i k m n p q	41, 42, 43, 44
42. CSO	c m p q	42, 38
43. Cl_2S	c m p q	28
44. Cl_2S_2	c m p q	28
45. CSC_2	c m p q	45, 46
46. SF_4	m p q	47
47. SOF_4	m p q	47
48. SO_2F_2	a c d g h k	48
49. SO_3	c m p q	49
50. H_2S_2	c m p q	28

TABLE 2

T (°K)	−ΔH° (kcal)	−ΔS° (e.u.)	−ΔG° (kcal)	log K
Reaction (1)				
298·15	25·59	29·38	16·83	12·3
400	26·55	21·47	17·96	9·8
500	25·86	21·58	15·07	6·6
600	26·17	21·07	13·53	4·9
700	26·36	21·10	11·59	3·6
800	26·59	21·21	9·62	2·6
900	26·78	21·02	7·86	1·9
1000	26·95	20·96	5·99	1·3
Reaction (2)				
298·15	55·33	23·52	48·32	35·4
400	55·29	21·52	46·68	25·5
500	55·52	21·17	44·93	19·6
600	55·02	21·34	42·22	15·4
700	54·64	20·95	39·97	12·5
800	54·17	20·38	37·87	10·3
900	54·04	20·83	35·29	8·6
1000	53·98	22·40	31·58	6·9

The oxidation of thia-alkanes

The first thermodynamic observations on the oxidation of thia-alkanes were made by Douglas,[31,32] who measured the heats of oxidation of 2-thiapropane to dimethyl

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TABLE 3

T° (K)	$-\Delta H^\circ$ (kcal)	ΔS° (e.u.)	$-\Delta G^\circ$ (kcal)	log K
298·15	53·15	21·86	46·63	34·2
400	52·81	20·88	44·46	24·3
500	52·49	20·14	42·42	18·5
600	52·19	19·61	40·42	14·7
700	51·94	19·22	38·49	12·0
800	51·74	18·98	36·56	10·0
900	51·60	18·77	34·71	8·4
1000	51·49	18·68	32·81	7·2

sulphoxide and dimethyl sulphone. Subsequently, Barrow and Pitzer[33] estimated the free energy changes associated with these reactions. Meanwhile the thermodynamic functions for dimethyl sulphoxide and dimethyl sulphone have been computed[30] more precisely and the heat, entropy, and free energy changes associated with reactions (1) and (2) are listed for a variety of temperatures in Table 2.

$$\mathrm{Me_2S(gas)} + \tfrac{1}{2}\mathrm{O_2(gas)} \longrightarrow \mathrm{Me_2SO(gas)} \qquad (1)$$

$$\mathrm{Me_2SO(gas)} + \tfrac{1}{2}\mathrm{O_2(gas)} \longrightarrow \mathrm{Me_2SO_2(gas)} \qquad (2)$$

In general, the gas-phase heat of oxidation of a thia-alkane to the corresponding sulphone:

$$\mathrm{R_1R_2S_{(gas)}} \longrightarrow \mathrm{R_1R_2SO_{2(gas)}} \qquad (3)$$

is independent of the nature of R_1 and R_2, provided these are saturated hydrocarbon groups. The reaction is exothermic to the extent of about 82 ± 2 kcal $\mathrm{mole^{-1}}$. About 30 kcal $\mathrm{mole^{-1}}$ are evolved in the first stage of the oxidation (to the sulphoxide) and the remaining 52 kcal $\mathrm{mole^{-1}}$ in the second stage. When $R_1 \equiv R_2 \equiv \mathrm{Ph}$ the exothermicity of reaction (3) is reduced to 77 kcal $\mathrm{mole^{-1}}$. It is further reduced to 70 kcal $\mathrm{mole^{-1}}$ when $R_1 \equiv R_2 \equiv \mathrm{Bz}$. On the other hand, it appears that, when $R_1 \equiv \mathrm{Me}$ and $R_2 \equiv \mathrm{Ph}$, the exothermicity of reaction (3) is increased to about 87 kcal $\mathrm{mole^{-1}}$. When diphenyl disulphide is oxidized to the corresponding disulphone 151 kcal $\mathrm{mole^{-1}}$ are evolved. This may be compared with twice the heat of oxidation, 154 kcal $\mathrm{mole^{-1}}$, of the corresponding monosulphide. The oxidation heats quoted above may be derived readily from the data given in Part I (Table 1).

Recently Goheen and Bennett[54] investigated the following nitric acid oxidation reactions:

$$\mathrm{2HNO_3 + 3RSR \longrightarrow 3RSOR + 2NO + H_2O} \qquad (3)$$

$$\mathrm{2HNO_3 + RSOR \longrightarrow RSO_2R + 2NO_2 + H_2O} \qquad (4)$$

Reaction (3) proceeds very readily with most oxidizing agents and apparently has a low activation energy. By contrast, reaction (4), although accompanied by a large heat evolution (see preceding paragraph), proceeds with much greater difficulty, and the activation energy is probably considerable. The reaction does not proceed at temperatures below 120°C.

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TABLE 4. THE THERMODYNAMICS OF SOME GAS-PHASE OXIDATIONS AND RADICAL REACTIONS

No.	Reaction	ΔH° (kcal)	ΔS° (e.u.)	ΔG° (kcal)	log K
1	$C_2H_5SH + 2O_2 \rightarrow CH_3CHO + H_2O + SO_2$	−158·9	−1·80	−158·0	68·61
2	$C_2H_5SH + 2\frac{1}{2}O2 \rightarrow CH_3COOH + H_2O + SO_2$	−223·7	−21·80	−212·8	92·40
3	$4C_2H_5SH + O_2 \rightarrow 2C_2H_5SSC_2H_5 + 2H_2O$	−105·7	−40·3	−85·6	37·17
4	$CH_3SH + CH_3O \rightarrow CH_3OH + CH_3S$	3·8	0	3·8	1·65
5	$CH_3S + CH_3S \rightarrow CH_3SSCH_3$	−65·6	−45·08	−38·1	16·54
6	$C_2H_5S + C_2H_5S \rightarrow C_2H_5SSC_2H_5$	−68·5	−45·87	−45·6	19·79
7	$CH_3CH_2SH \rightarrow CH_2 = CH_2 + H_2S$	18·5	30·63	−6·0	1·65

TABLE 5

Compound	ΔH_f° (kcal mole^{-1})	S° (e.u.)	Ref.
C_2H_5SH	−12·93	81·46	3
O_2	0	52·72	38
CH_3CHO	−41·18	71·14	57
H_2O	58·27	49·34	58
SO_2	−72·36	64·62	38
CH_3COOH	−106·0	77·5	59
$C_2H_5S_2C_2H_5$	−20·51	119·8	3
CH_3OH	−49·71	63·56	60, 61
$CH_3S_2CH_3$	−7·40	93·88	3
CH_3SH	−6·84	68·10	3
CH_3O	−2·1	64·94	*
CH_3S	29·1	69·48	*
C_2H_4	9·76	67·29	38
H_2S	5·86	57·99	1, 38

* These entropy terms were calculated using Barrow and Pitzers equations.[38]

The gas-phase oxidation of thiols

One hazard in the purification of thiols is their oxidation to dithia-alkanes via reaction (5).

$$2RSH + \tfrac{1}{2}O_2 \longrightarrow RSSR + H_2O \qquad (5)$$

The relevant thermodynamic data for the case where R ≡ Et are given in Table 3. They have been calculated using information available in a recent compilation,[3] and demonstrate that, at room temperature, the thermodynamic driving force for reaction (5) is quite high.

Four other thiol oxidation reactions have been postulated by Cullis and Roselaar.[56]

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These and the relevant thermodynamic quantities at 500°K, the temperature region of the experiments, are listed at the top of Table 4. Also included are the thermodynamic quantities for the related radical recombination reactions (5) and (6) and the pyrolysis reaction (7).[62] To calculate the above quantities we used data given in Table 5.

Gas-phase free radical reactions involving sulphur dioxide

Although there is considerable evidence for the addition of sulphur dioxide to alkyl radicals in the liquid phase, only preliminary investigations on the corresponding gas-phase reaction have been reported. Electron spin resonance experiments[64] indicate that trapped hydrocarbon polymer radicals react readily with gaseous sulphur dioxide at room temperature; the process can be reversed only by prolonged pumping under high vacuum. This indicates that the free energy change for the gas-phase reaction:

$$RSO_2 \longrightarrow R + SO_2 \qquad (6)$$

should be positive and fairly large. This has been calculated[65] for R ≡ Me, Et, n-Bu, t-Bu and the respective values are: $\Delta G = 13, 12{\cdot}6, 10$, and $6{\cdot}5$ kcal mole^{-1}. Thus the reversibility of the reaction becomes more pronounced as we proceed down the series. A similar situation exists for the process:

$$RS \longrightarrow R + \tfrac{1}{2}S_2 \qquad (7)$$

Here the ΔG-values down the same series are respectively[66]: 14, 11, 9 and 3·5 kcal mole^{-1}.

In the gas-phase oxidation of methyl mercaptan, Cullis and Roselaar[56] postulated the reaction:

$$CH_3S + O_2 \longrightarrow CH_3 + SO_2 \qquad (8)$$

and suggested that it proceeds by the following mechanism:

$$CH_3S + O_2 \longrightarrow CH_3SO_2 \qquad \Delta H_1 = -92 \text{ kcal}$$

$$CH_3SO_2 \longrightarrow CH_3 + SO_2 \qquad \Delta H_2 = +23 \text{ kcal}$$

The heats[65] associated with these steps are as listed. Thus the overall heat of reaction is -69 kcal mole^{-1}. This high exothermicity makes the above steps unlikely. As already discussed above, the equilibrium for the second step lies very much to the left-hand side.

There is little evidence that aromatic radicals react in the gas-phase with sulphur dioxide. However, Squire and Waters[67] have shown that phenyl radicals, produced in the reaction between benzoyl peroxide and benzene, combine quite easily with sulphur dioxide to give the benzene sulphonyl free radical $PhSO_2$. This is apparently too unreactive to combine with either benzene or chlorobenzene, but, when there are

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[67] J. M. Squires and W. A. Waters, *J. Chem. Soc.* 2068 (1962).

benzyl radicals present, rapid reaction occurs and phenyl benzyl sulphone is produced. These authors also showed that benzene sulphonyl radicals combine with each other to give diphenyl disulphone. This work substantiates the conclusions of Overrberger and Rosenthal[68] regarding the mechanism of decomposition of phenyl-phenylsulphonyl di-imide.

Sulphur dioxide, chlorine and a paraffin hydrocarbon react together[69] to give an alkane sulphonyl chloride, some chloroalkanes and polysulphonated materials. The following reaction scheme has been postulated.

$$\mathrm{Cl + RH \longrightarrow R + HCl} \tag{9}$$

$$\mathrm{R + SO_2 \rightleftharpoons RSO_2} \tag{10}$$

$$\mathrm{RSO_2 + Cl_2 \longrightarrow RSO_2Cl + Cl} \tag{11}$$

In the sulphochlorination of isobutane the product is entirely sec-butyl sulphonyl chloride. It has been suggested[69] that the absence of the t-butyl isomer is due to the high reversibility of the reaction:

$$\mathrm{tC_4H_9 + SO_2 \longrightarrow tC_4H_9SO_2} \tag{12}$$

We can calculate the free energy change for this at room temperature. We choose values of $-71{\cdot}0$,[1] 8[2], and -83 kcal mole^{-1} for $\Delta H_f(SO_2)_g$, $\Delta H_f(\text{t-Bu})_g$ and $\Delta H_f(\text{t-BuSO}_2)_g$ respectively and obtain a value of -20 ± 4 kcal mole^{-1} for the ΔH term. We compute the entropy term by applying the group incremental scheme of Barrow and Pitzer[70] as follows:

$$\begin{aligned} S^\circ(\text{t-BuSO}_2) &= S^\circ(\text{t-BuS}) + 2S^\circ(SO_3) - 2S^\circ(SO_2) + R \ln 9 \\ &= S^\circ(\text{t-BuSH}) + 2S^\circ(SO_3) - 2S^\circ(SO_2) + R \ln 18 \end{aligned}$$

Inserting values of 80·8,[66] 59·3[38] and 51·3[38] e.u. for $S^\circ(\text{t-BuSH})$, $S^\circ(SO_2)$, and $S^\circ(SO_3)$ at 298·2°K we find $S^\circ(\text{t-BuSO}_2) = 90{\cdot}6$ e.u. We obtain $S^\circ(\text{t-Bu}) = 70{\cdot}8$ e.u. by the method described by Trotman-Dickinson.[71] Thus for reaction (12) $S^\circ = -39{\cdot}5$ e.u. and $\Delta G^\circ = -8{\cdot}2 \pm 4$ kcal mole^{-1} at 25°C. Although the uncertainty is large, this result forces the conclusion that reaction (12) is not in fact significantly reversible at room temperature.

The therodynamics of the formation of polymeric sulphones from sulphur dioxide and alkenes have been investigated in some detail, notably by Dainton *et al.* at Leeds.[63] The heats of co-polymerization of sulphur dioxide with propylene, butene-1, hexene-1, hexadecene-1, *trans*-butene-2, *cis*-butene-2 and cyclopentene have been reported. Ivin *et al.*[72] have shown that the polymers formed from *cis*- and *trans*-butene-2 are identical. In discussing the kinetics and thermodynamics of the co-polymerization processes Dainton *et al.*[63] introduced the important concept of *ceiling temperature*, T_c, which relates the heat and entropy of co-polymerization in the following manner:

$$T_c = \frac{\Delta H}{\Delta S} \tag{13}$$

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[69] C. Walling, *Free Radicals. in Solution* p. 395. Wiley, New York (1958).

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[71] A. F. Trotman-Dickinson, *Gas Kinetics*. Butterworths, London (1955).

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It has been found that a change of structure, such as branching, mainly influences the heat term. In allyl compounds, a carbonyl group tends to lower T_c but an hydroxyl group has the opposite effect. The free energy change and reversibility of the co-polymerization reaction has been discussed by Busfield *et al.*[65] Hazell and Ivin[73] have examined the relative reactivities of a number of olefins in polysulphone formation, derived activation energies for the processes, and determined the heat of co-polymerization of cyclohexene and sulphur dioxide.

TABLE 6. FREE ENERGIES OF ISOMERIZATION AND EQUILIBRIUM CONCENTRATION RATIOS OF SOME SULPHUR CONTAINING MOLECULES IN THE IDEAL GAS STATE AT 298·15°K

Reaction	ΔH_i (kcal)	ΔS_i (cal deg^{-1})	ΔG_i (kcal)	Log K_i	C_1/C_2
$MeS(CH_2)_3Me \rightarrow EtSCHMe_2$	−3·8	−2·7	−2·99	2·19	0·993
$MeS(CH_2)_4Me \rightarrow EtS(CH_2)_3Me$	−1·2	0·6	−1·38	1·01	0·910
$EtS(CH_2)_3Me \rightarrow Me_2CH{\cdot}S{\cdot}CHMe_2$	−3·8	−8·6	−1·24	0·91	0·891
$Me_2CHSCHMe_2 \rightarrow EtSCMe_3$	−1·2	−0·2	−0·60	0·44	0·734
$Me_2CHCH_2SCH_2CHMe_2 \rightarrow Me_3CSCMe_3$	−6·7	−11·9	−3·20	2·35	0·996
$Me(CH_2)_4{\cdot}S{\cdot}(CH_2)_4Me \rightarrow Me_2CH(CH_2)_2{\cdot}S{\cdot}(CH_2)_2CHMe_2$	−4·0	−6·9	−1·90	1·39	0·961
$n{\cdot}Pr_2SO_2 \rightarrow t{\cdot}Bu{\cdot}SO_2{\cdot}Et$	−5·5	−7·7	−3·2	2·35	0·996
$n{\cdot}Bu_2SO_2 \rightarrow i{\cdot}Bu_2SO_2$	−4·1	−6·7	−2·1	1·54	0·972
$i{\cdot}Bu_2SO_2 \rightarrow t{\cdot}Bu_2SO_2$	−3·4	−11·9	0·1	−0·07	0·460
$n{\cdot}BuSO_2Me \rightarrow t{\cdot}BuSO_2Me$	−2·3	−9·2	0·5	−0·37	0·299
$n{\cdot}Pr_2SO \rightarrow t{\cdot}BuSO{\cdot}Et$	−4·6	−7·8	−2·3	1·69	0·980

Some equilibria involving organo-sulphur compounds

The equilibrium between two isomers can be evaluated provided ΔH_i, the heat, and ΔS_i, the entropy of isomerization are known. Thus the proportions of ethanethiol and 2-thiapropane in thermodynamic equilibrium have been established over a wide temperature range.[74] The equilibrium concentrations of the sulphur compounds found in petroleum have been derived[75,76] in an identical manner, as have the data listed in Table 6.[77] Where experimental values for the entropy terms were unavailable they were calculated by Barrow and Pitzer's group incremental method.[70] The entropy data for the linear thia-alkanes were taken from a recent compilation.[3] Other sources of information are indicated in Table 1. The heats of formation are listed in Part I[1] of this series.

Recently Haraldson *et al.*[78] have investigated the disproportionation equilibrium (14) between two symmetrical disulphides and the corresponding mixed one by gas-liquid chromatography.

$$R_1SSR_1 + R_2SSR_2 \leftrightharpoons 2R_1SSR_2 \tag{14}$$

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[73] J. E. Hazell and K. J. Ivin, *Trans. Faraday Soc.* **58**, 176 (1962).

[74] J. P. McCullough, W. N. Hubbard, F. R. Frow, I. A. Hossenlopp and G. Waddington, *J. Amer. Chem. Soc.* **79**, 561 (1957).

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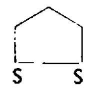
[76] W. N. Hubbard and G. Waddington, *Rec. Trav. Chim.* **73**, 910 (1954).

[77] H. Mackle and P. A. G. O'Hare, previously unpublished.

[78] L. Haraldson, C. J. Clander, S. Sunner and E. Varde, *Acta Chem. Scand.* **14**, 1509 (1960).

When $R_1 \equiv Me$ and $R_2 \equiv Et$ or i-Pr the equilibrium constant is close to four, the statistically predicted value. By contrast, when $R_1 \equiv Et$ and $R_2 \equiv$ t-Bu the equilibrium constant is twenty-four and temperature independent. Mackle and McClean have found zero strain energy in di-t-butyl disulphide, so steric strain is ruled out as a contributory factor. Furthermore, the value, 11 ± 3 kcal mole^{-1}, given in Part II[2] for $\Delta H_f(\text{t-BuS})_g$, in conjunction with the value,[79] $\Delta H_f°(\text{t-Bu}_2S_2)_g = -47{\cdot}1$ kcal mole^{-1} leads to a value of 69 kcal mole^{-1} for D(t-BuS-S-t-Bu) which is the same as D(EtS-SEt). It would thus appear that the abnormality is caused mainly by the entropy terms. This supports the argument of Haraldson *et al.*[78] which is as follows. The di-t-butyl disulphide molecule may be constructed from atomic models without introduction of strain from angle distortions and with a normal value (100°) for the dihedral angle. In this model, however, the two t-Bu groups are very close together and rotation around the C—S bonds is hindered. The free independent rotations of the t-Bu groups can be accomplished only when the dihedral angle exceeds 135°. On the other hand the intramolecular freedom in t-butyl ethyl disulphide is much greater. Thus the increased probability for the formation of the mixed disulphide in this case is caused by the "release" of conformations when the di-t-butyl disulphide molecule breaks up. Calvin *et al.*[80,81] have investigated the role of 6-thioctic acid in photosynthesis. Their argument rests upon the question of strain in the 1,2,-dithiolane ring. Because of the instability this ring system and its tendency to break and polymerize the strain cannot be measured by direct calorimetry, but Calvin *et al.*[80] have studied the equilibrium

$$RSSR + HS(CH_2)_3SH \rightleftharpoons 2RSH +$$



(15)

for R≡Bz and derived values of −1·67 kcal mole^{-1} and −1·75 kcal mole^{-1} for ΔG of the reaction at 24·1°C and 35·9°C respectively. These lead to a value of −6·3 kcal mole^{-1}, for the heat of the reaction. The authors concluded that the strain energy in 1,2, dithiolane, and likewise therefore in 6-thioctic acid, is at least 6·5 kcal mole^{-1} and probably larger, due to the repulsion of the sulphur lone-pair p-electrons. The question has been discussed in detail by Bergson and Schotte[82] who have shown that a strain energy as high as 24 kcal mole^{-1} is possible.

Barriers to internal rotation

Only for methanethiol[83] and 2-thiapropane[84,85] have the C—S bond rotational barriers been measured directly by microwave spectroscopy. A few of the barriers listed in Table 7 have been evaluated from observed infrared torsional frequencies. The great majority are based on the difference between observed and calculated heat capacities. Inspection of Table 7 shows that (1) the C—S barrier in thiols lies in the range 1·45 ± 0·2 kcal mole^{-1}; (2) for thia-alkanes the C—S barrier range is wider,

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TABLE 7. BARRIERS TO INTERNAL ROTATION (V) IN ORGANO-SULPHUR MOLECULES

Compound	V_0 (cal)	Reference no.
Methanethiol	1460 C—S	88, 89
	1270 C—S	83
Ethanethiol	1640 C—S	90
	3310 $C—CH_3$	
1-Propanethiol	1650 C—S	91
	3100 $C—CH_3$	
	2900 $C—C_2H_5$	
2-Propanethiol	1390 C—S	5
	3950 $C—CH_3$	
2-Butanethiol	1500 C—S	6
	4000 $C^2—C^1H_3$	
	3100 $C^3—C^4H_3$	
2-Methyl-1-propanethiol	1500 C—S	4
	3620 $C—CH_3$	
	5750 $C^1—C_4H_9$	
2-Methyl-2-propanethiol	1360 C—SH	6
	5100 $C—CH_3$	
Benzenethiol	0 C—S	9
2-Thiapropane	2000 C—S	84, 88, 92
	2100 C—S	
2-Thiabutane	1970 C—S	93
	3930 C—C	
3-Thiapentane	1750 C—S	94
	3550 C—C	
3-Methyl-2-thiabutane	2600 C—S	13
3,3,Dimethyl-2-thiabutane	2000 C—S	14
	4900 C—C	
2,3,Dithiabutane	1500 C—S	95
	6800 S—S	
3,4,Dithiahexane	3210 C—S	96
	13200 S—S	
2,Methylthiophene	900 C—S	23
3,Methylthiophene	600 C—S	24, 25
Dimethyl sulphoxide	2600 C—S	30

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TABLE 7 (contd)

Compound	V_0 (cal)	Reference no.
Dimethyl sulphone	2900 C—S	30
Thiolacetic acid	1500 C—S	28
	2500 C—C	
Methyl isothiocyanate	4700 C—N	28, 97
	910 C—N	
Thiourea	915 C—N	28
Sulphane	2700 S—S	98
	2000 S—S	28
Sulphur monochloride	5500 S—S	28

extending from 2·6 kcal $mole^{-1}$ in 3-methyl-2-thiabutane to 1·75 kcal $mole^{-1}$ in 3-thiapentane; (3) the S—S barrier in dithia-alkanes is of the same magnitude as that in sulphur monochloride but considerably larger than that for H_2S_2; (4) in thiophenol there is completely free rotation about the C—SH bond in marked contrast to the C—OH barrier of 3·14 kcal $mole^{-1}$ in phenol.[86] Comparison of barrier heights in thiols and thia-alkanes with their oxygen analogues[87] reveals corresponding dissimilarities.

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