Thermochemistry and Kinetics of Sulfur-Containing Molecules and Radicals

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Contents

I. Introduction

Sulfur is one of the abundant elements in the earth's crust. It is important in industry, in agriculture, in biology, and in air pollution. Because it occurs in crude oil to the extent of from 0.2 to 5.0% and in coals in the range of 0.2 to up to 10%, a great deal of research work has been directed to processes for the desulfurization of coal, oil, and fuels generally. An almost equal amount of work has been directed toward the removal of sulfur-containing species from the exhaust stacks of power plants and factories.[1] The increasing stringency of air quality standards has required a more sophisticated understanding of the chemistry and kinetics of sulfur-containing species, particularly at low concentrations. This has given rise to efforts to model the combustion and oxidation of sulfur compounds so as to better control both the production and the eventual removal of sulfur oxides.[2] Comparable efforts have been made to understand the detailed molecular steps whereby sulfur oxides in the ambient atmosphere become converted to sulfuric acid and visibility-reducing aerosol particles.[3]

One of the basic requirements in such modelling efforts is a detailed knowledge of the thermochemistry of the molecular and radical species which are involved in these steps. Such information is of importance both in interpreting some of the complex kinetic systems which have been studied and also in simplifying the oppressively large sequence of possible kinetic steps which may be significant in the molecular pathways for the overall reactions. It is the purpose of the present manuscript to attempt to review the relevant thermochemistry and select "best" values for use in analyzing the kinetic systems. Although the kinetics of air pollution and combustion involve mostly homogeneous gas-phase reactions, we shall see that the data taken from condensed phases will be of great utility and so our study will not be restricted to the gas phase. We shall review here all of the available thermochemistry on organic and relevant inorganic sulfur-containing molecules and radicals through 1976 and then more briefly the significant or controversial kinetic steps of importance in air pollution and combustion.

Our task in both these areas is enormously simplified by the availability of a number of recent surveys. Authoritative compilations of the thermochemistry of sulfur-containing molecules have been made by Cox and Pilcher[4] and by Stull, Westrum, and Sinke.[5] Perhaps the most detailed and critical evaluation on selected compounds comes from the JANAF series.[6] The NBS series of "Selected Values of Chemical Thermodynamic Properties", Technical Note 270-3,[7] is a valuable supplement to the preceding surveys, particularly for inorganic compounds, and we shall make extensive use of it. Unfortunately it is not documented and where possible we have gone back to the original literature sources. A critical survey of the thermochemical data on gas-phase organic species containing sulfur was published by the author and colleagues,[8] and we shall borrow heavily from this particularly for data on $S°$ and $C_p°$ and the methodology of group additivity.

Much less information exists on the heats of formation of sulfur-containing radicals. Mackle[9] made the first extensive survey of bond strengths in organic sulfur molecules, and some of these were included by Kerr[10] in his review of bond energies obtained by kinetic studies. Many were omitted by Kerr because of the "speculative" nature of the initial evidence. Much of this and subsequent data have been discussed and reevaluated by Benson and O'Neal in their monograph on unimolecular reactions.[11] Some of this has been in turn updated in a recent review.[12] In the present paper we shall also make use of kinetic data obtained from studies in condensed phases. Empirical rules can be employed to translate these data to equivalent gas-phase species albeit with some uncertainty. In a number of cases I have taken the liberty of revising reported kinetic *A* factors and have adjusted Arrhenius activation energies to maintain the rate constant at the observed value.

The format we have chosen to follow is to present and discuss the thermochemistry of divalent, then tetravalent, and finally hexavalent sulfur compounds. The relevant bond strengths will be treated in each appropriate section together with the radicals involved. The last section will treat the kinetics of oxidation processes. In what follows, all energies will be in kilocalories/mole while $C_p°$ and $S°$ will be in calories/mole·Kelvin (eu). In the tables to follow we have chosen to include a large number, but not all of the sulfur-containing compounds. Those species we have omitted may be found in one or more of the sources quoted, or else their thermochemical properties may be deduced by methods of group additivity from tables which have been published.[15] In Table XIII we list all the revised group estimates and new groups obtained in the present work.

II. Divalent Sulfur Compounds

The thermochemistry of divalent sulfur compounds seems to be fairly well established and very little new work has been done since the previous reviews.[4,5,8] Consequently, we shall use these values in our discussions. The thermochemistry of the organic divalent sulfur compounds seems not only reliable but also self-consistent in that it seems to follow empirical rules of group additivity[8] quite well. This is a considerable help to us since it means that we may employ group additivity rules with confidence to deduce the thermochemistry of species whose values have not been explicitly measured. The one exception to this rule seems to be the derivatives of ethylene sulfide where the apparent strain energy seems to depend on the amount of ring

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TABLE I. $\Delta H_f°_{298}$ and $S°_{298}$ of Some Molecules and Radicals of Divalent Sulfur[a,b]

Ref	Species	$\Delta H_f°_{296}$	(E strain)[b]	$S°_{296}$
6	S	66.3		40.1
6	S_2	30.7		54.5
19	c-S_3	32.5 ± 1	(22.9)	63 ± 1.5
19	c-S_4	31 ± 2	(18.4)	72 ± 2
7, 19	c-S_6	24.5	(5.3)	84.9
7	c-S_8	24.5	(−1.1)	103.0
6	SH	35 ± 1		46.7
7	H_2S	−4.9		49.2
	HS_2	[22.1 ± 1]		[61.4]
13a, 7	H_2S_2	3.8		62.3
	HS_3	[25.3 ± 1]		[74.8]
13a	H_2S_3	7.4		[75.7]
13a	H_2S_4	10.6		[89.1]
6	SO	1.2		53.0
	SOH	[5 ± 4]		[57 ± 1]
	$S(OH)_2$	[−67 ± 4]		[70 ± 1]
6	SF	3 ± 2		53.8
6	SF_2	−71 ± 3		61.6
	SCl	[36.5 ± 2]		57.3
7	SCl_2	−4.7		67.2
	SBr_2	[5 ± 4]		
6	FSSF	−80 ± 10		70.3
5	S_2Cl_2	−4.7		76.4
7	S_2Br_2(l)	−3		
	S_2Br_2(g)	[+9]		
48	SN	68 ± 5		53.1
28, 6	SC	64.8; 67 ± 6		50.3
6	CS_2	28.0		56.8
6	CSO	−33.1		55.3
26	$CH_2{=}S$	24.3		[56 ± 1]
14	CH_3S	34.2 ± 1.5		57.6
4	CH_3SH	−5.4		61.0
	$CH_2{=}CHSH$	[21.0 ± 2]		[67 ± 1]
	$CH_2{=}CHS\cdot$	[53 ± 3]		[62.0]
4	CH_3SCH_3	−8.9		68.3
7	C_2H_5SH	−11.0		70.8
14	C_6H_5S	56.8 ± 1.5		76.5
4	C_6H_5SH	26.7		80.5
7	c-CH_2CH_2S	19.7	(19.5)	61.0
4	$C_6H_5CH_2SH$	22.9		[91.0]
4	$(C_6H_5)_2S$	55.3		
	$CH_2(SH)_2$	[8 ± 2]		
	CH_3S_2	[17.3 ± 1]		
7	CH_3SSCH_3	−5.8		80.5
4	$C_6H_5SSC_6H_5$	58.4		
	CH_3SSS	[20.5 ± 1]		
	$CH_3S_4CH_3$	[0.4 ± 1]		
4	CH_3COSH	−43 ± 1		74.9
	HCOSH	[−30 ± 1]		
	$(CH_3O)_2S$	[−59 ± 5]		
	CH_3SCl	[−6.8 ± 1.5]		
	CH_3SSCl	[−5.1 ± 1.5]		
	C_6H_5SCl	[25.3 ± 1.5]		
	$C_6H_5S_2Cl$	[27 ± 1.5]		
8	$(NH_2)_2C{=}S$	−6.0		72.4
7	$HNC{=}S$	30.0		59.2
7	$CH_3NC{=}S$	31.3		69.3
7	CH_3SCN	38.3		[69 ± 1]
4	$[(C_2H_5)_2NS]_2$	−16.5 ± 1.5		
4	$(CNS)_2$	82.3		

[a] All species are ideal gas, standard states unless otherwise specified. $\Delta H_f°$ are in kcal/mol, $S°$ in cal/mol·K. Values in brackets have been estimated by the author; see text for details. [b] Values in parentheses are ring-strain energies.

substitution.[8] In consequence, these values may be considered uncertain to about ±2 kcal despite the good calorimetric precision in measuring their heats of combustion.

The group values which we shall use to estimate the thermochemistry of compounds not given here have been recently republished,[15] but some corrections based on recent studies are in order. The changes are as follows.

For the S–(C)(C$_d$) group we shall use the value $\Delta H_f°_{298} = 13.0$ kcal instead of the original 10.0 kcal. For the related group S–(H)(C$_d$) based on various analogies we derive the value $\Delta H_f°_{298} = 6.1$ kcal. For the S–(S)$_2$ group we use $\Delta H_f°_{298} = 3.2$ kcal (instead of 3.0). For thiacyclopentene-2 we assign a strain energy of 2.0 kcal rather than the value of 5.0 kcal, while for thiophene the value is not separable from the value of the group S–(C$_d$)$_2$. If we assign $\Delta H_f°$ for the latter as $\Delta H_f°_{298} = 13.5$ kcal rather than the −4.5 kcal originally assigned, to make for a more reasonable behavior of open-chain compounds, then it leads to a strain energy in thiophene of −16.3 kcal/mol which is a much more reasonable reflection of the appreciable resonance stabilization in this compound. Hence this −16.3 kcal/mol becomes the value to use as a ring correction to thiophene derivatives rather than the previous value of +1.7 kcal.

Table I lists values of $\Delta H_f°_{298}$ and $S°_{298}$ for key divalent molecules and related radicals containing sulfur. The values of $\Delta H_f°$ for S, S_2, and SO are derived spectroscopically and are probably reliable to ±0.1 kcal. The next radical of interest for us is the SH, and we have adopted the value shown of 35 ± 1 kcal. This comes from a reassessment of the kinetic data on $C_6H_5CH_2SH$, CH_3SH, and C_2H_5SH[11] and for once is in good agreement with data on electron impact. Of these three kinetic studies the first on $C_6H_5CH_2SH$ is the most reliable, but the extraction of a bond strength requires a scaling of the Arrhenius parameters to a reasonable A factor of about 10^{15} s^{-1} and an assignment of the scaled activation energy to the ΔE for the fission reaction. This latter is an important assumption which seems in good agreement with the best current data on radical recombination. It accounts for discrepancies of the order of about 1.5 kcal between the $\Delta H_f°$ for a number of radicals listed in ref 12 and the values listed in this paper and in ref 15. It also accounts for the much larger discrepancies between the $\Delta H_f°$ for CH_3S and C_6H_5S listed here and those in earlier reviews. The values listed here are from recent studies using VLPP techniques[14] which yield high-pressure kinetic parameters in excellent agreement with values of the absolute values of the rate constants from earlier studies[11] which employed the toluene carrier technique. The assignment of the observed, "scaled" activation energy to ΔE_T for the overall fission at reaction temperature together with a correction of ΔH_T to room temperature ΔH_{298} based on an estimated ΔC_p lead to a change from earlier values of about 4 kcal. It would be difficult to justify a change in the $\Delta H_f°_{298}$ for these radicals by more than the indicated uncertainties.

Kende et al.[16] have measured the rates of fission of $(CH_3S_2)_2$ in toluene at 65 °C using a radical scavenger to follow the first-order reaction.

$$(CH_3S_2)_2 \underset{-1}{\overset{1}{\rightleftarrows}} 2CH_3SS\cdot$$

They reported $kf = 5 \times 10^{17-36.6/\theta}$ s^{-1} where f is the efficiency with which the radicals are scavenged outside the initial cage and $\theta = 2.303RT$ (kcal/mol). Their A factor is too large by about 10^2 and since their temperature range was very limited (30 °C) we scale the Arrhenius paprameters to $A = 5 \times 10^{15}$ s^{-1} (comparable to peroxide fissions) and $E = 33.6$ kcal/mol. This latter value is in excellent agreement with values of 32.8 kcal for the S–S bond in liquid sulfur deduced from measurements of radicals in liquid sulfur.[17] We shall assume that the gas-phase value has the same value as has been frequently observed for the fission of nitrites and peroxides. Then using group additivity[15] to deduce a value for $\Delta H_f°_{298}(MeS_4Me) = 0.4$ kcal/mol we deduce the value of $\Delta H_f°_{298}(CH_3SS\cdot) = 17.3 \pm 1$ kcal/mol shown in Table I. This value together with group additivity yields the value $\Delta H_f°_{298}(HSS\cdot) = 22.1 \pm 1$ kcal/mol (Table I) and the values also shown in Table I for $HS_3\cdot$ and $CH_3S_3\cdot$.

TABLE II. Effect of Polarity and Electronegativity on Differences in Heat of Formation between Hydrogen (HX) and Methyl Derivative (CH_3X)[a]

X	ΔH_f°(HX)	ΔH_f°(CH_3X)	$\Delta(\Delta H_f^\circ)$	X	ΔH_f°(HX)	ΔH_f°(CH_3X)	$\Delta(\Delta H_f^\circ)$
F	−64.8	−55 ± 2	−9.8 ± 2	I	6.3	3.3	3.0
OH	−57.8	−48.0	−9.8	SCH_3	−5.4	−8.9	3.5
$O(SO_3)CH_3$	−170.5	−164	−6.5				
$O(CO)CH_3$	−103.8	−98	−5.8	C_2H_5	−20.2	−24.8	4.6
NH_2	−11.0	−5.5	−5.5	S_2H	3.8	−1.0	4.8
OCH_3	−48.0	−44.0	−4.0	*n*-C_3H_7	−24.8	−30.2	5.4
ONO_2	−32.1	−28.6	−3.5	C_2H_3	12.5	4.9	7.6
ONO	−18.3	−15.6	−2.7	C_6H_5	19.8	12.0	7.8
Cl	−22.0	−19.6	−2.4	NO	23.8	16	8
O_2H	−32.6	−31.3	−1.3	$COCH_3$	−39.7	−51.7	12.0
$NH(CH_3)$	−5.5	−4.5	−1.0	CN	32.3	[19 ± 2]	13 ± 2
Br	−8.7	−9.5	0.8	COOH	−90.5	−103.8	13.3
SH	−4.8	−5.4	0.6	CF_3	−167	−178	11
$N(CH_3)_2$	−4.5	−5.9	1.4	SiH_3	8	−4	12
CH_3	−17.9	−20.2	2.3	SnH_3	39	[28 ± 3]	11 ± 3

[a] All values in kcal/mol. Data taken from sources listed in Table I. Values in brackets are estimated by author.

Similar values have been obtained from the same data by Friswell and Gowenlock.[18] Note that we have used a slightly different value for the *S*–$(S)_2$ group than that listed in ref 15, namely $\Delta H_f^\circ{}_{298}(S\text{–}S_2) = 3.2$ kcal/mol. This is based on the ΔH_f° data for the sulfanes[13a,b] which indicate a very consistent value for this group up to H_2Sn6. This value for the *S*–$(S)_2$ group together with the observed value for c-S_3 (Table I) leads to a value of 22.9 kcal for the strain energy in the S_3 ring. This is comparable to values of 17.7 to 21 reported for the various ethylene sulfides.[8] Using this new group value we find strain energies of 5.3 kcal in the c-S_6 ring and −1.1 kcal in the c-S_8 ring.

A very useful guide to thermochemistry comes from consideration of the relative electronegativity of bonds. The SH group and Br atoms are expected to have similar electronegativities and similar radii, and, in fact, the dipole moments of HBr and H_2S are 0.82 and 0.97 D, respectively,[20] while the H–Br and H–S bond lengths are 1.415 and 1.345 Å, respectively.[21] CH_3Br and CH_3SH have similar dipole moments of 1.81 and 1.52 D, respectively,[20] the C–S and C–Br bond lengths in these compounds are 1.82 and 1.93 Å, respectively,[21] and as we shall also see there are close similarities in the bond dissociation energies in these compounds. A thermochemical datum which also parallels the electronegativities of atoms X is the difference in the values of ΔH_f° for the compounds HX and CH_3X.

It is observed that when X changes from a very electronegative element to a very electropositive element, the difference $\Delta H_f^\circ(\text{HX}) - \Delta H_f^\circ(\text{CH}_3\text{X})$ changes from a negative to a very positive quantity. This type of relation appears to hold true whether or not X is a single atom or part of a more complex group. A typical range of values for this difference is illustrated by the data in Table II. It can be seen from Table II that neighboring groups can exert an important influence on these differences. An excellent example is provided by CH_3 and CF_3. Similarly, while CH_3 for H substitution in HOH makes ΔH_f° more positive by 9.8 kcal, a second CH_3/H substitution increases ΔH_f° by only 4.0 kcal. The same influence of substitution is seen in the nitrogen series and in the sulfur family. This influence of nonbonded, next-nearest neighbors has been rationalized as arising from a change in effective charge on the central atom[22–25] and hence its polarity.

As the polarity of the central atom goes from very negative to very positive values the CH_3/H substitution covers a range of from −10 to +14 kcal/mol. Such a relation permits us to estimate ΔH_f° for compounds with uncertainties of about ±2 kcal/mol. Thus we can estimate for the unknown H–NO_2 isomer of nitrous acid (HONO) a $\Delta H_f^\circ = -6 \pm 2$ kcal/mol based on the known $\Delta H_f^\circ(\text{CH}_3\text{NO}_2) = -17.9$ kcal/mol. This accounts very well for the inability to prepare this isomer since it is about 12 kcal less stable than HONO for which $\Delta H_f^\circ = -18.3$ kcal/mol and in which the H atom is likely to be quite labile.

Such analogies permit us to estimate ΔH_f° for $CH_2(SH)_2$ from the value of CH_2Br_2 as 6 ± 2 kcal (Table I). We shall make frequent use of these relations and for convenience we shall refer to groups which show similar thermochemical behavior as homothermal. The *n*-alkyl groups CH_3, ethyl, *n*-propyl, etc., form a homothermal family. From the relations in Table II we would estimate that R–SH compounds, where R has about the polarity of carbon compounds, would differ in ΔH_f° from R–Br compounds by 4.0 ± 0.3 kcal. This is true for R = H, CH_3, and C_2H_5 (Table II) and appears to be true for R–C_2H_3 for which the $\Delta H_f^\circ(\text{C}_2\text{H}_3\text{SH})$ has been estimated by other methods. It is therefore somewhat surprising that the ΔH_f° of phenyl compounds differ only by 1.7 kcal since vinyl and phenyl have about the same kind of carbon atoms.[23] However, the uncertainty in $\Delta H_f^\circ(\text{C}_6\text{H}_5\text{Br})$ is at least 2.0 kcal and may be the source of the apparent inconsistency. $\Delta H_f^\circ(\text{CH}_3\text{COBr})$ is 2.6 ± 1.5 kcal lower than $\Delta H_f^\circ(\text{CH}_3\text{COSH})$ which is well within the expectations of our Br/SH substitution rule.

Using the H/CH_3 substitution value observed for HCOOH and CH_3COOH (Table II) we can deduce $\Delta H_f^\circ(\text{HCOSH}) = -30 \pm 1$ kcal shown in Table I.

In the first long row of the periodic table one of the rather startling early observations on bond dissociation energies[27] was the weakness of the single bonds between the isoelectronic groups NH_2, OH, and F. These are among the weakest single bonds in the periodic table and decrease uniformly in the sequence CH_3–CH_3 (88), NH_2–NH_2 (70), HO–OH (50), F–F (38). There is a comparable decrease in bond strengths in the related sequence in the second-row SiH_3–SiH_3, PH_2–PH_2, HS–SH, Cl–Cl, but the bonds range from 0 to 20 kcal stronger than their first-row group analogues. This tendency has been rationalized on electrostatic grounds as arising from the repulsion of nonbonded lone pairs. In molecular orbital terms the equivalent explanation comes from the increasing destabilization of antibonding electrons. The increased bond strengths in the symmetrical second-row compounds are then explained on the basis of a decreased repulsion of the lone-pair electrons arising from their greater separation in the larger radius, second-row elements. This larger radius of the second-row elements compared to first-row elements should also lead to both weaker σ and π bonds when the lone-pair effects can be eliminated. As we shall see, the data reflect this, but the effects are much smaller than might have been anticipated.

In Table III we list the few compounds containing S atoms double bonded to some other atom or group. The S bond dissociation energies in these compounds are compared with that of their oxygen analogues. We first notice that the S–S bond in S_2 is some 17 kcal weaker than the O–O bond in O_2. As expected from considerations of both electronegativity difference

TABLE III. Comparison of Double Bond Strengths in Some Divalent Sulfur Compounds with Oxygen Analogues

Sulfur compd	X=S bond dissociation energy	Oxygen analogue	X=O bond dissociation energy
S_2	102.5	O_2	119.2
SO	124.7	OS	124.7
SC=S	103.4	SC=O	157.5
CH_2=S	129 ± 5	CH_2=O	172 ± 3
OC=S	73.3	OC=O	127.2
C=S	173	C=O	257
CH_3NC=S	71	CH_3NC=O	[133 ± 4]

TABLE IV. Some S-H Bond Dissociation Energies for Divalent Sulfur

RS-H[a]	Bond dissociation energy	RS-H[a]	Bond dissociation energy
·S-H	83.6 ± 1	HS_2-H	70 ± 1.5
HS-H	92.0 ± 1	Alk-S_2-H	70 ± 1.5
CH_3S-H	92 ± 1.5	HS_3-H	70 ± 1.5
C_2H_5S-H	92 ± 2	HS_{3+n}-H	70 ± 1.5
Alk-S-H	92 ± 2	Alk-S_{3+n}-H	70 ± 1.5
C_6H_5S-H	82 ± 1.5		
·S_2-H	60.5 ± 1.5		
CH_2=CHS-H	[84 ± 2]		

[a] Alk = alkyl.

and lone-pair repulsion the bond dissociation energy in SO is greater than in either homonuclear molecule.

Even larger differences exist in the CH_2O and CH_2S pair where there is no lone-pair repulsion and in the CO, CS pairs which are really better described as triple bonded compounds.

A measure of the relative abilities of S and O atoms to donate electrons and act as Lewis bases is seen on comparing the C-O bond strengths in CH_2O with CO_2. The 45 kcal apparent smaller OC=O bond strength in the latter compound can be associated with the extra π bond formation in CO. The greater C-O bond strength in SCO compared to OCO is then a reflection of the weaker base properties of S in C=S. The same behavior is seen in the sulfur analogues. The CH_2=S bond is stronger than the SC=S bond while the OC=S bond is one of the weakest S bonds we shall observe.

In the sequence CO_2, COS, CS_2 there is a constant 61 kcal change in $\Delta H_f°$ on replacing O by S. This difference is maintained in the related pair of very polar compounds $CO(NH_2)_2$ and $CS(NH_2)_2$ for which data exist in aqueous solutions[7] and suggests that it should be the same in the paired compounds CH_3NCO/CH_3NCS and HNCO/HNCS. On this basis we would assign $\Delta H_f°_{298}[HNCO(g)] = -30$ kcal. This would make it about 6 ± 2 kcal/mole more stable than the isomeric HOCN.[7]

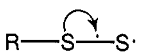
In Table IV we list some S-H bond dissociation energies derived from the data on $\Delta H_f°$ shown in Table I and the known $\Delta H_f°$ of H and other free radicals (ref 15). A number of features are noteworthy. In the saturated monosulfur compounds RS-H the S-H bond is 92 kcal, independent of the nature of R. In the oxygen homologues a similar behavior is seen except in the case of HOH where the O-H bond has a value of 119 kcal in contrast to ROH compounds where it is 104 kcal. This is a reflection of the polarity effects already discussed in connection with Table II.

Phenyl exerts a bond weakening effect on adjacent S-X bonds analogous to its effect on CH_2 and O reflecting a delocalization of the ring electrons and charge donation to the radical center. The effect in $C_6H_5S\cdot$ measured against saturated RS· radicals is seen to be 10 kcal, significantly lower than the 13.5 kcal observed in $C_6H_5\dot{C}H_2$ and the 17 kcal found in $C_6H_5O\cdot$.[29] As we shall see, this is a reflection of the weaker π bond between C and S.

TABLE V. Some S-C Bond Dissociation Energies for Divalent Sulfur

RS-C	Bond dissociation energy	RS-C	Bond dissociation energy
·S-CH_3	66 ± 1.5	CH_3S-CH_3	77 ± 1.5
·S-C_2H_5	63 ± 2	Alk-S-CH_3	77 ± 1.5
·S-Alk	63 ± 2	C_6H_5S-CH_3	67.4 ± 1.5
·S-C_6H_5	88.5 ± 1.5	CH_3S-C_2H_5	74 ± 1.5
		n-Alk-S-C_2H_5	74 ± 2
HS-CH_3	75 ± 1.5		
HS-C_2H_5	72 ± 1.5	*n*-Alk-S-*i*-Pr	73.5 ± 1.5
HS-*i*-Pr	71 ± 1.5	*n*-Alk-S-*t*-Bu	71 ± 1.5
HS-*t*-Bu	69 ± 1.5	CH_3S-C_6H_5	89.2 ± 2
HS-C_2H_3	83 ± 3	CH_3S-CN	97 ± 1.5
HS-C_6H_5	86.5 ± 2		
HS-(CO)H	74 ± 2	HS_2-CH_3	57 ± 1.5
HS-$COCH_3$	73 ± 2	Alk-S_2-CH_3	57 ± 1.5
·S_2-CH_3	47.5 ± 1.5	Alk-S_2-C_2H_5	54 ± 1.5
·S_2-C_2H_5	44.5 ± 1.5	Alk-S_2-C_6H_5	69.5 ± 1.5
·S_2-C_6H_5	60 ± 2	Alk-S_n-C_2H_5	54 ± 1.5

Sulfur also exerts a bond weakening influence on adjacent bonds, and we see that the S-H bond in the higher sulfanes H_2S_{n+1} is some 22 kcal weaker than the other S-H bonds. This difference can be identified with the partial double or π bond formed in the radical



and reflects the Lewis base character of divalent sulfur. It can be compared with the similar behavior of O atoms in H_2O_2 where the effect relative to ROH is about 14 kcal.[27]

The behavior of the S-H bond strengths is also paralleled by the S-C bonds listed in Table V. Saturated groups R attached to S have little or no influence on the adjacent RS-CXYZ bond for a given X, Y, and Z. Unsaturated groups R or groups with lone pairs or conjugated π electrons exert a bond weakening effect comparable to their effect on S-H bonds. Of particular interest for the symmetrical compounds X_2S is the observation that the first bond dissociation energy is about 8.5-11.0 kcal stronger than the second. This is opposite in behavior to the oxygen analogues R_2O where the second bond in RO· is about 8 kcal stronger than the first bond. This inverse behavior can again be seen as arising from polarity effects on the $\Delta H_f°$ of the two sets of compounds R_2O and R_2S. We note from Table II that the substitution of CH_3 for H in H_2O and CH_3OH increases $\Delta H_f°$ while the opposite is the case for CH_3/H substitution in H_2S.

Adjacent sulfur atoms again have a bond weakening effect on S-C bonds. From Table V we see the bond lowering is 20 kcal compared to 22 kcal for the S-H bonds. In principle these two numbers should be the same and within the experimental uncertainty we can represent them by their average of 21 ± 1 kcal. This is a measure of the relative self-consistency of the $\Delta H_f°$ data for both the molecule and radical species involved and the application of group additivity. We find a similar consistency on comparing the S-Cl bond strengths in MeS-Cl and MeS_2-Cl (Table VI). The heats of formation of these mixed compounds have been estimated by methods of bond additivity from $\Delta H_f°$ for SCl_2 and S_2Cl_2. The difference in these two bond strengths is estimated at 19 ± 3 kcal in good agreement with the 21 ± 1 kcal difference calculated for the S-H and S-C series. However, on comparing the similar S-S bonds in H_2S_2 and H_2S_2 and H_2S_3 (Table VI) we find a difference of only 16 ± 2.5 kcal with a similar value for the HS_2-S_2H/HS_2-SH difference. These are real discrepancies and reflect the fact that H_2S does not follow the bond additivity rules followed by other sulfanes but is instead more stable by almost 6 kcal.

Sulfur-sulfur bonds follow the same general trends we have noted for the S-H and S-C bonds. They are, however, significantly stronger in the alkyl disulfides than in the hydrogen disulfanes (Table VI). This effect disappears after R_2S_4 and thus is strictly a neighboring S–S effect.

Very few other S bond strengths are known, and Table VI lists the ones that have been measured. A number of S–Cl bonds have been estimated by additivity methods plus the observation that the first R–S bond dissociation energies exceed the second in the R_2S_2 compounds by about 9.5 ± 1 kcal.

This last observation which appears to hold for R = H, alkyl, aryl, SH, SCH_3, and Cl gives us a handle on the strength of the π bond in S_2 and related compounds. The difference between the first and second bond dissociation energies in symmetrically substituted alkanes RCH_2CH_2R can be equated to the π bond energy formed in the C_2H_4 product.[27] It has been shown to be a transferable quantity independent of the groups R.[30] In the case of unsymmetrical olefins or heteronuclear olefins such as $CH_2{=}O$ or $HN{=}O$ or $CH_2{=}NH$, we need to know the bond strengths in the two possible radicals, for example, $CH_3O\cdot$ and $\cdot CH_2OH$. For symmetrical π bonds there may be significant stabilization in the intermediate radical as in the radicals $RS_2\cdot$. This leads to weakening of the first bond in RS_2–R and strengthening in the second bond in R–$S_2\cdot$ and hence a smaller difference $DH°_1 - DH°_2$ by double the amount of stabilization in the radical.

If we adopt the stabilization energy in $RS_2\cdot$ as 21 ± 1 kcal, then the π bond strength in S_2 can be estimated as the nearly universal $DH°_1 - DH°_2 = 9.5 \text{ kcal} + 2 \times 21 = 51.5 \pm 2$ kcal. A similar calculation for peroxides yields a value of 71 ± 1.5 kcal for the π bond strength in O_2. This latter is very reasonable compared to π bond strengths observed in olefins (~60 kcal), acetylenes (~72 kcal), and aldehydes (~76 kcal).

We can apply the same reasoning to the relation between CH_3SH and $CH_2{=}S$. From Table I we can estimate the sum of the C–H and S–H bonds that are broken in the process as 133.5 ± 3 kcal. The S–H bond we know to be 92 kcal (Table IV) while the C–H bond is not known. In fact, we anticipate that it will be weakened by the adjacent S atom relative to the C–H bond in ethane. If we adopt a value of 98 kcal for a hypothetically unperturbed C–H bond strength in CH_3X then we estimate 190 kcal as the sum of the C–H + S–H bonds in CH_3SH in the absence of interactions. The difference between this value and the experimental 133.5 ± 3 can then be taken as the π bond strength in CH_2S, namely, 56.5 ± 3 kcal. This is very close to the value of the π bond strength in olefins and is consistent with the observation that $\Delta H_f°(CH_2{=}S)$ is very closely the average of $\Delta H_f°$ for S_2 and C_2H_4. The average is 21.6 kcal/mol compared to the 24 ± 3 reported (Table I).

The above value of the $C{=}S$ π bond strength is only 3 ± 3 kcal lower than the values observed in olefins and can be used to rationalize the fact noted earlier that $C_6H_5S\cdot$ has a stabilization energy about 3.5 kcal lower than found in $C_6H_5{\cdot}CH_2$ which is in turn about 3.5 kcal weaker than the value found in $C_6H_5O\cdot$. On this basis we would predict that the S–H bond strength in $CH_2{=}CHSH$ will be about 84 kcal reflecting an estimated 8 kcal "allylic" stabilization energy in the $CH_2{=}CHS\cdot$ radical.

The pyrolysis of divalent sulfur compounds has proven fairly difficult of interpretation. Part of this difficulty has come from the occurrence of parallel radical and molecular paths[11] as well as appreciable sensitivity to vessel wall condition and traces of oxygen. Compounds containing π bonds to sulfur are extremely susceptible to polymerization[26,31] and this is generally a heterogeneous process probably acid and/or base catalyzed. One difficulty that has not been appreciated arises from reactions producing elementary sulfur as a product[32] such as in the pyrolysis of episulfides which produce olefins plus sulfur.

TABLE VI. Some S–S and Other Bond Dissociation Energies for Divalent Sulfur

RS–SR′	Bond dissociation energy	RS–X	Bond dissociation energy
HS–SH	66 ± 2	$\cdot$S–F	82 ± 3
CH_3S–SCH_3	74 ± 2	FS–F	92 ± 3
Alk-S–S-Alk	74 ± 2	CH_3S–Cl	[70 ± 3]
		CH_3S_2–Cl	[51 ± 2.5]
HS_2–SH	50 ± 2	ClS_2–Cl	[51 ± 2]
HS_2–SCH_3	54 ± 2	$\cdot S_2$–Cl	[42 ± 2]
HS_2–S-Alk	54 ± 2	C_6H_5S–Cl	[31 ± 2.5]
HS_2–SC_6H_5	44 ± 2	ClS–Cl	[70 ± 3]
		$\cdot$S–Cl	[60 ± 2]
		BrS–Br	[62 ± 4]
HS_2–S_2H	33.6 ± 2	$\cdot$S–Br	[52 ± 4]
Alk-S_2–S_2-Alk	33.6 ± 2	BrS_2–Br	[42 ± 4]
RS_{2+n}–$S_{2+m}R$	33.6 ± 2	$\cdot$S–OH	[70 ± 4]
		HOS–OH	[81 ± 4]
HS–S$\cdot$	79 ± 1	$C_6H_5N{=}N$–SC_6H_5	[29 ± 1][62]
CH_3S–S$\cdot$	83 ± 1	$(Ar)_3CS$–NO	[25 ± 1][63]
C_6H_5S–S$\cdot$	74 ± 1.5	CH_3S–NO	[25 ± 1]
FS–SF	61 ± 4		
C_6H_5S–SH	61 ± 1.5		
C_6H_5S–SCH_3	65 ± 1.5		
C_6H_5S–SC_6H_5	55 ± 1.5		
RS_2–S$\cdot$	63 ± 1		
RS_2–$S_2\cdot$	47.5 ± 1		

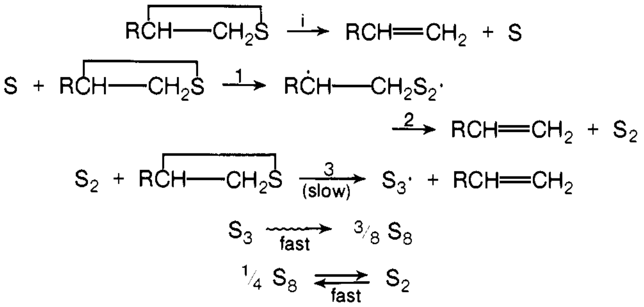
The stable form of sulfur in the gas phase is S_8 if it is below its vapor pressure. But the equilibrium

$$c\text{-}S_8 \overset{a}{\rightleftarrows} 4S_2$$

is readily attained and leads to a small but significant and almost constant concentration of the very reactive S_2 species:

$$(S_2) = K_{eqa}^{1/4}(S_8)^{1/4}$$

Since (S_2) is proportional to $(S_8)^{1/4}$, a fourfold change in (S_8) gives only a 40% change in (S_2). ΔH_a = 24.7 kcal and one can calculate from the data in Table I that at 500 K 1 Torr of S_8 will be in equilibrium with 2.5 mTorr of S_2. It is very likely that the apparent first-order thermal decomposition of episulfides proceeds by a complex chain reaction in which the rate-determining step is bimolecular:



The rate constant for sulfide disappearance is then:

$$-d(RC_2H_3S)/dt = k_i(RC_2H_3S) + k_3K_a^{1/4}(S_8)^{1/4}(RC_2H_3S)$$

where after a very brief induction period during which S_2 and S_8 build up, the first term becomes negligible and $(S_8)^{1/4}$ varies only slightly. A value of E_3 in the range 11–14 kcal would then account quite well for the observed apparent first-order rate constants. Reaction 3 is close to being thermoneutral for most R and presumably goes through a biradical R-ĊH-$CH_2S_3\cdot$ intermediate. It is also therefore reversible and might show a resultant inhibiting effect on the overall reaction as product olefin is produced, which might then obscure the small autocatalytic effect due to increasing S_8.

A final observation is in order regarding the strain energies in small ring compounds containing sulfur. Compared to first-row ring compounds containing C, O, N where strains seem to be dependent only on ring size, we note that rings with a single s atom have about 8 kcal less strain than the carbon analogue.

TABLE VII. Heats of Formation and Entropies of Some Molecules and Radicals of Tetravalent Sulfur

Ref	Species	$\Delta H_f^\circ{}_{296}$	$S^\circ{}_{296}$	Ref	Species	$\Delta H_f^\circ{}_{296}$	$S^\circ{}_{296}$
(6)	SO_2	−70.9	59.3		SO H_2	[−16 ± 4]	
				(4)	$SO(Me)_2$	−36.0	73.2
(7)	$SO_2(aq)$	−77.2	38.7	(6)	SSF_2	[<−60 ± 6]	70.0
						−96 ± 10	70.0
(2, 6)	S_2O	−10	63.8	(6)	SF_3	−119 ± 4	66 ± 1.5
(6)	SOF_2	−130 ± 5	66.7	(4)	$SO(Et)_2$	−49.1	
(7)	$SOCl_2$	−51	74.0	(4)	$SO(C_6H_5)_2$	25.6	
(7)	$SOBr_2$	−21.8		(4)	$SO(NEt_2)_2$	−66.3	
(6)	SF_4	−183 ± 5	71.6		$S{=}S(Me)_2$	[4 ± 3]	
(7)	$SO(HO)_2(aq)$	−145.5	55.5		$S{=}SH_2$	[10 ± 7]	
	$SO(HO)_2$	[−127 ± 3]	[69]		CH_2SO	[−12 ± 5]	
(4)	$SO(OMe)_2$	−115.5			$HOSO(O_2H)$	[−105 ± 5]	
(4)	$SO(OEt)_2$	−131.9					
60	$C_6H_5S(SO)C_6H_5$	[34 ± 2]					
60, 64	C_6H_5SO	[13 ± 2]					
	$(C_6H_5SO)_2$	[11 ± 4]					
(4)	$C_6H_5CH_2SOC_6H_5$	20.6					

TABLE VIII. S=S and S=O Bond Dissociation Energies in Sulfoxide Derivatives

Species	Bond dissociation energy	Species	Bond dissociation energy
$S{=}O$	124.7	$H_2S{=}O$	[71 ± 4]
$OS{=}O$	132	$Me_2S{=}O$	86.6
$SS{=}O$	100	$Et_2S{=}O$	88.7
$F_2S{=}O$	118 ± 6	$CH_2{=}S{=}O$	[95 ± 5]
$(HO)_2S{=}O$	[118 ± 6]	$(C_6H_5)_2S{=}O$	89.3
$(MeO)_2S{=}O$	[116 ± 6]		
		$OS{=}S$	77
$Cl_2S{=}O$	105	$F_2S{=}S$	[>57 ± 8]
$Br_2S{=}O$	[86 ± 4]	$Me_2S{=}S$	[53 ± 4]
$C_6H_5\dot{S}{=}O$	[103 ± 2]	$H_2S{=}S$	[51 ± 7]
$C_6H_5SSOC_6H_5$	[83 ± 4]		
$C_6H_5SOSOC_6H_5$	[83 ± 4]		

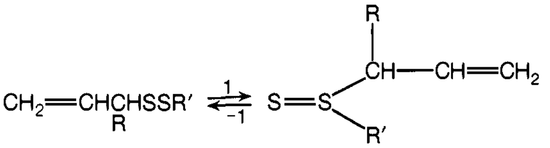
Surprisingly this seems to hold true for rings with three or four sulfur atoms as well.

III. Tetravalent Sulfur

The higher valence states of sulfur are conspicuous by the fact that they are known only in the form of oxygen or fluorine derivatives, and these can be classified as derivatives of $>SO$ or $>SF_2$ in the tetravalent states or $>SO_2$, $>SOF_2$, and $>SF_4$ derivatives in the hexavalent states. As such they are strongly reminescent of the noble gas compounds and the higher valence states of the halogens. Relatively little is known about the thermochemistry of the tetravalent sulfur compounds and most of this is of lower quality than that for divalent sulfur. Most of the data available are shown in Table VII. One of the important compounds in this table is sulfurous acid for which $\Delta H_f^\circ(aq)$ is well known although there is still some uncertainty as to how much H_2SO_3 in aqueous solution is better considered as the isomer $H_2O{\cdot}SO_2$. Based on data for differences in ΔH_f° between gas phase and aqueous solutions for comparable species we have estimated a difference of 18.5 ± 3 kcal for the two phases. This gives a value for the gas-phase species that appears to be consistent with other related values.

An interesting example of the effect of electronegative species on the relative stability of the two and four valence states of sulfur is seen in the isomeric compounds FSSF and SSF_2. Both of these compounds can be prepared, presumably pure.[33] However, if the liquid FSSF is allowed to warm up above 0 °C it spontaneously changes over to the more stable SSF_2. In contrast dialkyl disulfides RSSR[1] appear only to be stable and known in the indicated bonding state. However, there is substantial evidence indicating that the isomeric thiosulfoxide form SS(R)R′ is probably not more than 10 kcal less stable.

Höfle and Baldwin[34] have convincingly demonstrated that allyl disulfides can undergo a Cope-type rearrangement with a thiosulfoxide intermediate



This intermediate can be trapped by $P(C_6H_5)_3$ to give $SP(C_6H_5)_3$ and $R'SCHRCH{=}CH_2$. At high enough concentrations of the trapping agent $P(C_6H_5)_3$, the reaction is observed to be first order with $\Delta H^\ddagger = 20 \pm 1$ kcal and $\Delta S^\ddagger = -9 \pm 1$ eu. If the $P(C_6H_5)_3$ reaction is assumed to have an activation energy of about 3 to 4 kcal, then the thiosulfoxide must lie not more than 10 kcal in heat of formation above the disulfide. This then leads to the estimates for $\Delta H_f^\circ[S{=}S(Me)_2]$ and $\Delta H_f^\circ(SSH_2)$ shown in Table VII. It is interesting to speculate that, since the relative stability of thiosulfoxides seems to shift with the electronegativity of the groups attached to S, compounds like $(RO)_2S{=}S$ might be stable relative to their disulfide isomers while somewhere in the sequence Br_2S_2, Cl_2S_2 one might find the two isomeric forms close together in ΔH_f° and hence coexisting. Both forms $(RO)_2S{=}S$ and ROSSOR are known.[66]

The only bonds for which dissociation energies are known with any certainty are some of the S=O double bonds and these are tabulated in Table VIII. Along with them we have listed the less certain S=S bonds in thiosulfoxides. It can be seen that as the electronegativity of the groups attached to the tetravalent sulfur decreases, the S=O bond strength decreases along with it. The same behavior, although with much less certainty, is displayed by the S=S bonds in thiosulfoxides. A possible exception to this is the observation by Mislow and Miller[64] that optically active aryl-SO-CH_2-aryl will racemize with a rate constant much larger than for nonbenzylic type substituents. From the observed *A* factor and observation of radical recombination products they deduce, in fact, that the racemization is proceeding via a bond fission. If we take their rate constant and an assigned *A* factor of $10^{15.5}$ s^{-1}, we can estimate an activation energy of 36 kcal. Assuming the same value in the gas phase and neglecting substituent effects in the aryl groups then permits us to estimate $\Delta H_f^\circ(C_6H_5SO{\cdot})$ as shown in Table VIII. The bond strengths deduced in this fashion are reasonably consistent with those deduced by other methods as will be seen in the following.

The best we can do under these conditions is to list the sum of the two bonds dissociation energies and perhaps speculate on how they may differ. This is shown in Table IX. They show the same decrease in binding energy with electronegativity that we

TABLE IX. Sum of Single Bond Dissociation Energies R–S + R′–S in Sulfoxides RR′S=O and Thiosulfoxides and Estimates of D_1[a]

Species	$D_1 + D_2$	Est D_1	Species	Sum of bond dissociation energies	Est D_1
F_2SO	169	(87)	H_2SO	121 ± 4	(63)
Cl_2SO	110	(58)	Me_2SO	105	(55 ± 2)
Br_2SO	75	(40)	Et_2SO	102	(54)
[F_2SF_2	105 ± 6	(83 ± 5)]	$(C_6H_5)_2SO$	133	66 ± 2
$(HO)_2SO$	146 ± 3	(76)			
$(MeO)_2SO$	125	(65)	F_2SS	[>129 ± 6]	
$(EtO)_2SO$	125	(65)	Me_2SS	95 ± 3	(47 ± 3)
$(Et_2N)_2SO$	122	(63)	H_2SS	125 ± 7	(64 ± 7)
$C_6H_5S–SOC_6H_5$		36[b]	C_6H_5SO		67 ± 2

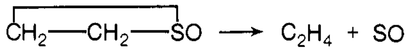
[a] Values in parentheses indicate estimated value of D_1 based on $D_1 - D_2 = 5 \pm 2$; see text. [b] This value differs from that reported of 34.5 kcal. The value of 36 kcal is derived from a revision of the experimental *A* factor. See text.

have already seen in the S=O and S=S bond strengths.

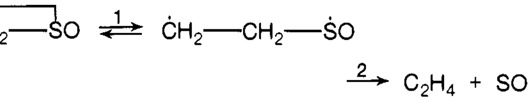
The general tendency in the sulfur bond strengths that we have considered so far is for the first of a pair of identical ligands to be more strongly bound than the second. The one datum that exists in the tetravalent sulfur group is for successive S–F bonds in SF_4. From the data in Table VII we may estimate the first bond dissociation energy as 83 ± 5 while the second becomes 67 ± 5, the difference being 16 kcal in favor of the first. On the other hand, for the thiosulfoxides of CH_3 and H we can estimate the first bond dissociation energies from the data in Table IX, and they suggest within the large uncertainties shown that $D_1 \approx D_2$, although a difference $D_1 - D_2 \sim 8 \pm 3$ would also be compatible with the data.

Data on the pyrolysis of Me_2SO which is a radical chain process[35] can be employed to yield a value of $DH°(CH_3\text{–}SO(CH_3))$ $\geqslant 53$ kcal but $\leqslant 56$ kcal. If we take the mean as 55 ± 2 kcal then $DH_2°(Me\text{–}SO) = 50 \pm 2$ kcal which is in reasonable accord with the preceding observations on Me_2SS and SF_4. It would suggest $D_1 - D_2 \sim 5 \pm 1$ kcal in Me_2SO which in turn suggests that this might be applicable to the other sulfoxides as well.

Additional information comes from the pyrolysis of ethylene sulfoxide[36] which decomposes to ethylene + SO_2 + S in chlorobenzene solution at 100 °C. The activation energy was estimated at 36 kcal/mol. However, the overall reaction to eliminate SO



is only endothermic by about 25 kcal if we assume the strain energy to be like that in the episulfide, namely 18 kcal/mol. If we utilize our assumption that in R_2SO, $D_1 - D_2 = 5 \pm 1$, then in Et_2SO the C–S bond strength is 53 kcal. Thus the activation energy for ring opening to the biradical is only 34 kcal/mol



The second step in this process is exothermic by 11 kcal and probably has very little activation energy, thus making step 1 rate determining. If ring closing has only a few kilocalories of activation energy, the data would be compatible with the observations. A concerted process cannot be ruled out. It would be spin forbidden and involve a crossing of the singlet–triplet surface at an appreciably higher activation energy than the overall endothermicity.

Qualitative rate data can be extracted from observations on the temperature required for the pyrolysis of trimethylene sulfoxide[37] to give $CH_2{=}SO + C_2H_4$. These are also in agreement with the biradical mechanism, reaction starting with C–S bond fission to give the unstable $\cdot(CH_2)_3\dot{S}O$ biradical.

From these estimates of R–SOR′ bond strengths we can also obtain an estimate of the π bond strength in CH_2SO. Starting with CH_3SOCH_3 we can estimate the sum of the $CH_3\text{–}SOCH_3$ (55 ± 2) and the C–H in the "unperturbed" methyl (98 kcal) as 153 ± 2 kcal. But the overall reaction

$$CH_3SOCH_3 \rightarrow CH_2{=}SO + H + CH_3$$

is endothermic by 110 ± 5 kcal. Hence the C–S π bond strength in $CH_2{=}SO$ is 43 ± 5 kcal, appreciably less than the π bond strength of 56.5 we have calculated for $CH_2{=}S$. This appears surprising since microwave studies[37] have shown identical C–S bond distances in CH_2S and CH_2SO. However the π bond estimates or $\Delta H_f°$ would have to be uncertain by over 10 kcal to bridge this gap. Even worse the required changes in $\Delta H_f°$ and E_π would have to be in unacceptable directions. Thus $CH_2S{=}O$ has an unusually high DH° compared to other alkyl sulfoxides (Table VIII). If this were lowered by making the differences in $\Delta H_f°$ of CH_2SO and CH_2S smaller, the difference in π bond strengths would increase.

It is interesting to note that the C_6H_5SO radical has an estimated stabilization energy of only 3 kcal, considerably less than the 9.6 kcal observed in C_6H_5S and also less than the 13 found in $C_6H_5SO_2$. This would be in accord with the weak π bond formation in $CH_2{=}SO$ just commented on.

IV. Hexavalent Sulfur

Hexavalent sulfur compounds can all be represented as derivatives of the $>SF_4$ or $>SO_2$ groups and they are presented in this fashion in Table X. The data are again very meager compared to that for divalent sulfur compounds, and their accuracy, with few exceptions, is not better than ±2 kcal.[8] To interpret oxidation kinetics we would like to know thermochemical data for the oxy and peroxy molecules and radicals in this series and here the data are particularly sparse. However, a number of empirical rules will be of assistance to us. The first is that F and OH turn out to be a homothermal pair. The replacement of OH by F in compounds where the attachment is to an electronegative element X ($RXOH \rightarrow RXF$) results in an increase in $\Delta H_f°$ of about 7 kcal. For X = H or CH_3 this reverses to −7 kcal. When X is more positive as in vinyl, phenyl, or carbonyl compounds, substitution of F for OH makes $\Delta H_f°$ more negative by about −2 kcal. SO_2 can be fitted into this sequence by observing that $SO_2(OH)_2$ is 4 kcal less stable than SO_2F_2 while $FSO_2(OH)$ is almost precisely the arithmetic mean.

Thus the SO_2 group seems to follow bond additivity rules to about ± 1 kcal with respect to elements of similar electronegativities such as Cl, F, and OH. On this basis we have estimated $\Delta H_f°$ for $Cl(SO_2)OH(g)$ as −133 ± 1 kcal (Table X). This appears to be compatible with the known $\Delta H_f°$ for the liquid and $\Delta H_{vap}°$ extrapolated from $F(SO_2)OH$ (Table X).

Data on the peroxy sulfuric acids exist only in aqueous solution. If we use the 40 kcal difference between $\Delta H_f°(aq)$ and $\Delta H_f°(g)$ for H_2SO_4 as a starting point for extrapolation and

TABLE X. Heat of Formation and Entropies of Some Molecules and Radicals of Hexavalent Sulfur

Ref	Species	$\Delta H_f^\circ{}_{298}$	$S^\circ{}_{296}$
(6)	SO_3	−94.6	61.3
(6)	SO_2F_2	−181 ± 2	67.8
(6)	SO_2Cl_2	−84.8 ± 0.5	74.3
(6)	SO_2ClF	[−133 ± 5]	72.3
(6)	SF_6	−291.7	69.7
	SF_4Cl	[−177]	
(6)	SF_5	[−218 ± 3]	77 ± 2
(6)		−233 ± 5	
(7)	SF_5Cl	−250.5	76.3
(4)	SO_2H_2	[−64 ± 4]	
(7, 6)	$SO_2(OH)_2$ (l)	−194.5	37.5
	(aq)	−217.3	4.8
	(g)	−177.0 ± 2	69.1
	SF_5OH	[−290 ± 2]	
(6)	$FSO_2(OH)$ (l)	−190.5	
	(g)	−180	71.0
(7)	$ClSO_2(OH)$ (l)	−143.7	
	(g)	[−133 ± 1]	
	$F(SO_2)O\cdot$	[−127 ± 1.5]	[68.5 ± 1]
	$HO(SO_2)O\cdot$	[−125 ± 2.0]	[72 ± 1]
	SF_4Cl_2	[−205 ± 3]	[78 ± 1.5]
	$\cdot SO_3H$	[−98 ± 3]	[67 ± 1]
(4)	$SO_2(Me)_2$	−88.7	74.2
	$SO_2(Me)$	[−55]	
(4)	$SO_2(OMe)_2$	−164	
(4)	SO_2Ph_2	−28.3	
(4)	$SO_2(OEt)_2$	−180.7	
(4)	$SO_2(Et)_2$	−102.5	
(4)	$PhSO_2\text{–}SO_2Ph$	−115	
	SO_2CH_2	[−69 ± 3]	
	$c\text{-}(SO_2O)_3$	−314	
	$HO(SO_2)O_2H$ (aq)	[−192 ± 2]	
	(g)	[−152 ± 2]	[81.5 ± 1]
(7)	$[HO(SO_2)O]_2$ (aq)	−320	59.3
	(g)	[−272 ± 2]	[104 ± 2]
(7)	$HO(SO_2)_2OH$ (aq)	−286.4	
	(g)	[−246 ± 5]	
	$[F(SO_2)O]_2$ (g)	[−276 ± 3]	[101 ± 2]
	$[HO(SO_2)]_2O$	[−282 ± 3]	
	$c\text{-}O_2\overline{S\text{–}O\text{–}O}$	[−76 ± 3]	
	Biradical SO_4	[−73 ± 5]	
	$HOSO_2O_2\cdot$	[−114 ± 4]	
	$SO_2(O_2H)_2$	[−127 ± 3]	
(60, 61)	$C_6H_5SO_2$	[−37 ± 1]	
(60)	$C_6H_5(SO_2)SOC_6H_5$	[−52 ± 2]	
	$C_6H_5(SO_2)SC_6H_5$	[−22 ± 4]	
	$SF_5O\cdot$	[−236 ± 4]	
65	SF_4O	[−226 ± 4]	
	$(SF_5O)_2$	−509 ± 5	

consider that $H_2S_2O_8$ is a very strong acid like H_2SO_4, then we estimate an aqueous — gas difference of 47 ± 3 kcal for $H_2S_2O_8$ and assign to $H_2S_2O_8$ a value of $\Delta H_f^\circ(g) = 273 \pm 3$ kcal shown in Table X. This value together with group additivity gives a value of −153 ± 2 kcal for $\Delta H_f^\circ(HO(SO_2)OOH)_{gas}$. Further assuming that H_2SO_5 has a difference in ΔH_f° between gas and aqueous states similar to H_2SO_4 leads to $\Delta H_f^\circ(H_2SO_5)_{aq} = -193 \pm 3$ kcal.

Monger and Redlich[38] have measured the equilibrium

$$H_2SO_4 + HO_2H \rightleftarrows H_2SO_5 + H_2O$$

in aqueous solution and found an apparent equilibrium constant of about 0.1 at 25 °C which increased to about 0.2 at 75 °C. This latter would suggest $\Delta H \approx +2.8$ kcal and require $\Delta S \cong 5$ eu to account for $\Delta G \approx 1.4$ kcal. This would lead to $\Delta H_f^\circ(H_2SO_5)_{aq} = 188$ kcal in only fair agreement with our previous estimate. However, the best a priori estimates of ΔS° for this equilibrium yield a value of $\approx +13$ eu and hence a $\Delta H \approx -2.8$ eu. The increase in K_{eq} with T would then have to be ascribed to an anomalously high value for ΔC_p°. This latter choice would give $\Delta H_f^\circ(H_2SO_5)_{aq} = -193$ kcal, in excellent agreement with the earlier estimate. A reasonable reconciliation would be to use −191 ± 2 kcal which leads then to $\Delta H_f^\circ{}_{298}(H_2SO_5)_{(gas)} = -151 \pm 3$ kcal and thence via group additivity to $\Delta H_f^\circ{}_{298}(H_2S_2O_8)_{(gas)} = -270 \pm 6$ kcal. As a reasonable compromise among these values we shall use $\Delta H_f^\circ{}_{298}(H_2S_2O_8)_{(gas)} = -272 \pm 2$ kcal. This then leads to $\Delta H_f^\circ{}_{298}(H_2SO_5)_{(gas)} = -152 \pm 2$ and the other related values shown in Table X.

TABLE XI. S=O Bond Dissociation Energies in Hexavalent Sulfur Species

Species	Bond dissociation energy	Species	Bond dissociation energy
$O_2S{=}O$	83.3	$Me_2SO{=}O$	112
$F_2SO{=}O$	110 ± 5	$Et_2SO{=}O$	112
$Cl_2SO{=}O$	95	$Ph_2SO{=}O$	113
$(HO)_2SO{=}O$	110 ± 3	$PhSO{=}O$	109
$(MeO)_2SO{=}O$	108	$(PhSO_2)PhSO{=}O$	122
$(EtO)_2SO{=}O$	109	$(PhSO)PhSO{=}O$	122 ± 3
$[F_4S{=}F_2$	146 ± 5]	$(PhS)PhSO{=}O$	115 ± 4
$SF_4{=}O$	102 ± 6	$CH_2SO{=}O$	[116 ± 6]

Let us note in passing that a similar equilibrium study of formic acid[38]

$$H_2O_2 + HCOOH \rightleftarrows H_2O + HCO_3H$$

leads to a value for $\Delta H_f^\circ(HCO_3H)_{gas}$ in excellent agreement (±1 kcal) with independent estimates from group additivity and kinetic data on diacyl peroxides.[39]

Now making use of our observation that F and OH form a homothermal pair relative to SO_2 with a $\Delta(\Delta H_f^\circ)$ of 2 kcal we can estimate $\Delta H_f^\circ[F(SO_2)OO(SO_2)F]_{gas} = -276 \pm 3$ kcal.

A number of studies have been made of the reversible dissociation of $F_2S_2O_6 \rightleftarrows 2FSO_3\cdot$[40] and ΔH and ΔS are known with reasonable accuracy. From these measurements and the data already discussed we estimate $\Delta H_f^\circ(FSO_3\cdot)_{gas}$ and $S^\circ(FSO_3\cdot)$ shown in Table X as well as the other entropies shown. Finally using our F/OH rule we estimate $\Delta H_f^\circ(HOSO_3\cdot)_{gas} = -125 \pm 2.0$ kcal. Note that this yields a value for the O–H bond dissociation energy in H_2SO_4 of 104 ± 3 kcal. This can be compared with DH°(RO–H) of 104 kcal in all the aliphatic alcohols and 106 kcal for DH°(RCO_2–H). If we assume that the second O–H bond dissociation energy in H_2SO_4 is not affected by removing the first, then we can calculate for the SO_4 biradical $\Delta H_f^\circ(SO_4) = -73 \pm 4$. This has some very interesting consequences which we shall pursue later in our discussion of the kinetics of SO_2 oxidation. For the moment let us simply note that SO_4 is a stable biradical with an O_3S–O bond dissociation energy = 28 ± 4. At 25 °C we should expect SO_4 to be a long-lived species. It has a more stable cyclic analogue $O_2\overline{S\text{–}O\text{–}O}$ whose $\Delta H_f^\circ{}_{298}$ we can estimate from known groups and an assigned strain energy of 18 ± 2 kcal as −77 ± 2. Whereas SO_4 biradical can be triplet or singlet, the cyclic three-membered ring isomer can only be singlet.

If we use an assumption which has been very successful in treating organic hydroperoxides ROOH, namely that the O–H bond dissociation energy is the same as in H_2O_2, viz. 90 ± 1 kcal, then we can estimate that $\Delta H_f^\circ{}_{298}[HO(SO_2)OO\cdot]_{gas} = -114 \pm 4$ kcal and that this radical is stable relative to dissociation into $HOSO_2\cdot$ radical + O_2 by only 16 ± 5 kcal. This implies that this radical is probably a very important intermediate in photochemical smog involving sulfur-containing species.

Bond dissociation energies for the double bonded O atoms in sulfone derivatives are tabulated in Table XI. They seem surprisingly insensitive to the substituents on the central group with the exceptions of Cl_2SO_2 and SO_3. All of the other values

TABLE XII. X–SO_2 Single Bond Dissociation Energies in Sulfone Derivatives

Species	Bond dissociation energy	$D_1 + D_2$	Species	Bond dissociation energy	$D_1 + D_2$
$CH_3(SO_2)$–CH_3	68	86	SO_2F_2	[100]	148
$Et(SO_2)$–C_2H_5	68	84	SO_2Cl_2	[63]	75
$CH_3(SO_2)$–allyl	55	73	$SO_2(OH)_2$	[88]	125
$CH_3(SO_2)$–benzyl	56	74	$SO_2(F)(OH)$		136
$C_6H_5(SO_2)C_6H_5$	70	114	$SO_2(HO)(O_2H)$		95
$CH_3(SO_2)$–C_6H_5	83	101	$[F(SF_4)$–F	93 ± 3	147]
$C_6H_5(SO_2)$–CH_3	54	101		79[46]	147 ± 3[46]
$C_6H_5SO_2$–$SO_2C_6H_5$	41 ± 1				
$C_6H_5SO_2$–SOC_6H_5	28 ± 1				

can be approximated as 111 ± 2 kcal. The exceptional stability of SF_6 is indicated by the high value of 146 ± 5 for removing two F atoms.

If we compare these $R_2SO{=}O$ bond dissociation energies with the values for $R_2S{=}O$ (Table VIII), we note that they are uniformly less by about 8 kcal for electronegative R. Even for the $SO_2Cl_2/SOCl_2$ pair this relation holds. This is not the case for the alkyl sulfones where the $DH°(R_2S{=}O)$ are uniformly less by about 23 kcal than $DH°(R_2SO{=}O)$. One consequence of these relations is that the four-valent states of sulfur will be unstable with respect to disproportionation when the ligands to S are alkyl or aryl groups while the opposite will be true for electronegative groups. As examples of this tendency we have

$$2C_6H_5SOC_6H_5 \rightleftarrows C_6H_5SC_6H_5 + C_6H_5SO_2C_6H_5 + 24\ \text{kcal}$$

$$2CH_3SOCH_3 \rightleftarrows CH_3SCH_3 + CH_3SO_2CH_3 + 26\ \text{kcal}$$

$$2F_2SO \rightleftarrows SF_2 + SO_2F_2 - 7\ \text{kcal}$$

$$2Cl_2SO \rightleftarrows SCl_2 + SO_2Cl_2 - 10\ \text{kcal}$$

Kice[60] has noted the "bond-weakening effect" of SO on adjacent bonds ascribing the effect to the stability of the $R\dot{S}O$ radicals. From the above as well as from data we shall present later on bond strengths, we conclude that the instability actually arises from the $\Delta H_f°$ of the parent molecule and for the sulfones and sulfoxides illustrates again the principle of alternating polarity[22,25] which is so important in determining thermochemical stability. We have, in fact, noted that the $C_6H_5\dot{S}O$ radical has less stabilization energy than $C_6H_5S\cdot$ or $C_6H_5\dot{S}O_2$.

There are very few direct measurements of single bond dissociation energies for hexavalent sulfur compounds. Mackle and colleagues[11] used toluene carrier techniques to measure the rates of pyrolysis of alkyl and aryl sulfones. However, their assignments of Arrhenius parameters were inconsistent and usually too low. Reinterpretation and scaling of their Arrhenius parameters using presently available thermochemical data lead to the bond dissociation energies shown in Table XII.

The data on the alkyl sulfones are self-consistent within ±2 kcal which is about the reliability of the $\Delta H_f°$ data. From complex kinetic studies of the radiolysis of CH_3SO_2Cl in cyclohexane, Horowitz[41] has evaluated K_{eq} for

$$MeSO_2 \overset{1}{\rightleftarrows} Me + SO_2$$

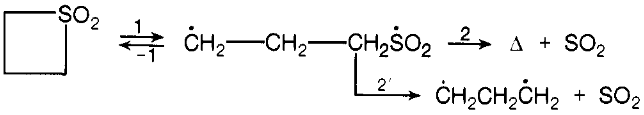
in the range 60–122 °C and from its temperature coefficient the values $\Delta H°_1$ = 15.6 kcal/mol and $\Delta S°_c$ = 23 eu. In the gas phase $\Delta S_p°$ = 35 eu so that we could estimate that $\Delta H°$ = 17.2 kcal/mol would be the appropriate value for the gas phase dissociation in excellent agreement with the data in Table XII.

Further corroborating evidence for both these bond dissociation energies comes from the work of Good and Thynne[47] who measured the direct gas-phase equilibrium between $CH_3 + SO_2$. They found ΔH_1 = 20 ± 2 while values for the equilibrium

$$C_2H_5 + SO_2 \overset{1'}{\rightleftarrows} C_2H_5SO_2$$

gave $\Delta H_{1'}$ = −17 ± 1 kcal/mol, in excellent agreement with our estimate of 16 ± 2 (Table XII). Interestingly, they claimed to observe activation energies of about 3 kcal/mol for both of these addition reactions and find them both very much slower than the same radical reactions with O_2. This would tend to support the analogy between CO (or CO_2) and SO_2. CO has an appreciable reorganization energy of about 75 kcal and shows a small activation energy for radical or atom addition which varies with the electronegativity of the radical.

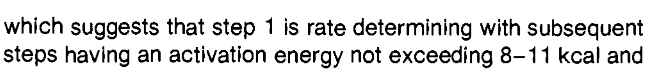
Cornell and Tsang[42] have conducted toluene carrier studies of the pyrolysis of trimethylene sulfone and 2-methylsulfolane. Very interestingly, for the former they find only cyclopropane and only traces of propylene, suggesting that trimethylene is not an intermediate. The high A factor of $10^{16.1}\ s^{-1}$ and E_{act} = 56 ± 1 kcal suggest an open ring, very loose transition state. Assuming 19 kcal strain energy for the ring we estimate 49 kcal for the ΔH of ring opening to form the biradical:



If reaction 2 which is 38 kcal exothermic has a loose transition state for the S_N2 displacement of SO_2 from C by the free radical end and an activation energy of 7 kcal, this would be compatible with the observations. The competing reaction 2′ to form trimethylene + SO_2 with a 16 kcal activation energy and a higher A factor would still be about tenfold slower than reaction 2, and this is in agreement with the very small amount of propylene found.

A third competing path for the biradical, which is also exothermic, is to split into $C_2H_4 + CH_2{=}SO_2$. From the lack of excess C_2H_4 products we must conclude that the activation energy for this step exceeds 12 kcal. C_2H_4 production from the sulfone could not be measured in the system because of the use of ethyl acetate → $CH_3COOH + C_2H_4$ as an internal standard reaction to monitor the temperature.

Their study of 3-methylsulfolane yields again a high A factor suggestive of a loose transition state and an activation energy of 66.4 kcal. We can estimate a value for $\Delta H_1 \approx 63 \pm 2$ kcal



which suggests that step 1 is rate determining with subsequent steps having an activation energy not exceeding 8–11 kcal and a high A factor on the assumption that $E_{-1} \sim 3$ kcal with an expectedly low A factor of about $10^{12}\ s^{-1}$. Since the energy to detach SO_2 from the biradical requires some 15 kcal, this is a barely possible intermediate step. It is not unlikely that the

TABLE XIII. Some Revised and New Group Values for Use in Group Additivity Estimates

Group	$\Delta H_f°_{296}$	Group	$\Delta H_f°_{296}$
$S-(C_d)_2$	13.5	$O-(H)(SO_2)$	-38.0^a
$S-(C)(C_d)$	13.0	$O-(H)(S)$	-38.0^a
$S-(H)(C_d)$	6.1	$O-(H)(SO)$	-38.0^a
$S-(S)_2$	3.2	$O-(SO_2)_2$	-4
$S-(O)_2$	$+9 \pm 4$	$O-(O)(SO_2)$	3
		Ring corrections	
$SO-(O)_2$	-51 ± 3	Thiophene	-16.3
$SO_2-(O)_2$	-101	Thiacyclopentene-2	2.0
$SO_2-(F)(O)$	-142	c-S_3	22.9
$SO_2-(Cl)(O)$	-97	c-S_4	18.4
		c-S_6	5.3
		c-S_6	-1.1

[a] These are assigned values in accord with usual conventions.

biradical cleaves into the three final species with an activation energy appreciably lower than this. Alternatively, we might expect a displacement reaction similar to that observed for the trimethylene sulfone. Its parameters are in the range of interest and would lead to methylcyclobutane as a metastable intermediate which decomposes about threefold faster than the sulfone. The authors actually found a C_5 product which they could not identify which amounted to about 10% of the decomposition and could well be the cyclobutane derivative.

Recent[67] stereochemical studies on the pyrolysis of *cis*- and *trans*-1,2-dimethylsulfolanes have shown about 20–30% retention of configuration in the product butene-2. This would rule out a concerted path for the process and favor a biradical path with slow internal rotation competing with cleavage. This could almost require a concerted split of the biradical into three fragments rather than consecutive cleavage or intermediate cyclobutane formation.

On this basis we derive the values for D_1 for the sulfones shown in Table XII. If we now consider $D_1 - D_2$ for the symmetrical sulfones, we find it has the value 50 ± 2 kcal which can be considered a reorganization energy of the SO_2 group. While there is no reason to expect this to be a constant independent of R in R_2SO_2, we can note that it is consistent with one of the few directly measured values of $F-SO_2F$ from shock tube studies.[43] The authors fitted their data using RRK theory to bond strengths of 81 and 95 kcal/mol. They chose the former as giving a better fit to their data. However, the number of degrees of freedom and their *A* factor were unjustifiably small. More acceptable values for the latter yield higher values for E_0 closer to 100 kcal when extrapolated back to room temperature.

This latter value gives $D_1 - D_2 = 52 \pm 2$ kcal in good agreement with the other sulfones. Assuming that this difference applies to SO_2Cl_2 we estimate DH°($ClSO_2-Cl$) = 63 shown in Table XII. In similar fashion reanalysis of the shock tube data on SF_6 leads to a F_5S-F bond dissociation energy at room temperature of 93 kcal[44] which is also compatible with electron impact and electron affinity data on SF_6 and SF_5.[45] This differs appreciably from the values selected by Hildenbrand[46] and the subject deserves further study. Note, however, that it yields $D_1 - D_2 = 39$ for the SF_4 series.

Assignment of the constant difference for SO_2R_2, $D_1 - D_2 = 50 \pm 2$ yields the bond strengths DH°($HOSO_2-OH$) = 88 kcal shown in Table I and $\Delta H_f°(\dot{S}O_2OH) = -98$ kcal.

The $\Delta H_f°$ deduced for the substituted SO_3 radicals permits us to draw some conclusions concerning SO_3. From the data in Table X we can estimate DH°($F-SO_2O\cdot$) = 51 ± 1.5 kcal and DH°($HO-SO_2O\cdot$) = 39 ± 2 kcal. From $\Delta H_f°(HO\dot{S}O_2) = -98 \pm 3$ we can calculate an H–O bond dissociation energy of 81 kcal for the first bond in H_2SO_3 and a value of a value of 55 kcal for DH°[$H-O\dot{S}O_2$]. This gives 26 kcal as the reorganization energy of the isomeric SO_3 biradical $\dot{O}-SO-\dot{O}$ to SO_3. This permits us to calculate the R–O bond dissociation energies in the sulfites $(RO)_2SO$. From the data in Table VII we find 89 kcal for $D_1 + D_2$ for $CH_3-OSO_2CH_3$ and using $D_1 - D_2 = 26$ kcal we estimate $D_1 = 57.5$ kcal and $D_2 = 31.5$ kcal.

DH°($HO-\dot{S}O_2$) = 36 kcal which is only slightly weaker than the attachment of the OH bond to SO_3.

In H_2SO_5 we can estimate the O–O bond strength as 36 kcal, appreciably stronger than the 22 kcal we estimate for the O–O bond in $H_2S_2O_8$ but typical of the differences in O–O bond strengths between peroxides and hydroperoxides. While $\Delta H_f°[HO(SO)O_2H]_{gas}$ is not known, we can estimate upper and lower limits for it from $\Delta H_f°$ of the sulfone analogue $HO(SO_2)O_2H$ and the $>S{=}O$ bond dissociation values listed in Table XI. For polar species OH, OR, and F or even alkyl and aryl substituents this bond is 111 ± 2 kcal. For the O substituent it is 15 kcal lower. With one OH and one OOH substituent we can guess that 107 ± 4 might well bracket all likely values and thus give $\Delta H_f°(HO(SO)O_2H)_{gas} = 105 \pm 5$ kcal. This would make the O–O bond dissociation energy in this compound only 16 ± 6 kcal, from which we would conclude that the acid is unstable at temperatures above 200 K. This is the weakest of O–O bonds in the entire sequence.

An interesting bond strength is the central O–S bond in pyrosulfuric acid $HOSO_2-O-SO_2OH$. For this bond we estimate DH°($HOSO_2-OSO_3H$) = 59 ± 5 kcal which explains why the various polymeric forms of SO_3 are quite stable in the absence of an acid or base catalyst.

The observation[60,61] that the $C_6H_5SO_2-SO_2C_6H_5$ bond fission has an activation energy of 41 kcal in inert solvents permits us to estimate $H_f°(C_6H_5SO_2\cdot)$ (Table XII) and a stabilization energy in this radical of 14 ± 1 kcal, very similar to the stabilization energy in $C_6H_5CH_2\cdot$ of 13 kcal. The stabilization observed in $C_6H_5S\cdot$ is some 4.5 kcal less than that in $C_6H_5SO_2$, and this is probably to be expected since the source of the stability is the donation of charge from C_6H_5 to the SO_2 group and the latter is much more electrophilic than S. From these values we may expect that the π bond strength of carbon to SO_2 may be somewhat greater than C to S. If we assign a value of 60 ± 3 kcal to this π bond, then we can estimate DH°($O_2\dot{S}CH_2-H$) = 38 ± 3 kcal and $\Delta H_f°(CH_2{=}SO_2) = -69 \pm 3$ kcal mol. This seems compatible with the S=O bond dissociation energies in similar compounds (Table XI).

For dithionic acid $H_2S_2O_6$ where $\Delta H_f°$ is known only approximately, we estimate DH°($HOSO_2-SO_2OH$) = 50 ± 10 kcal. One would anticipate from the analogy with $(C_6H_5SO_2)_2$ that a more negative $\Delta H_f°$ and a stronger bond closer to 60 kcal would be more likely.

One of the more interesting compounds of sulfur is the SO_4 discussed earlier. The cyclic form is stable relative to the decomposition into $SO_2 + O_2$ by about 5 ± 3 kcal but might have a high activation energy for such a decomposition because of spin forbiddeness. It is marginally more stable than the biradical SO_4 by about 3 ± 5 kcal. The SO_4 biradical is stable relative to decomposition into $SO_3 + O$ by 38 kcal and also stable relative to decomposition into $SO_2 + O_2$ by 2 ± 5 kcal. If SO_4 is a stable or metastable species, however, this latter mode of decomposition is probably restrained by dynamic considerations rather than energetic ones.

There is good experimental evidence for believing that SO_4 biradical is a stable species in the gas phase. Westenberg and deHaas[49] have shown that at room temperature O atoms and SO_3 add together in a very rapid termolecular reaction with rate constants that can only be rationalized if there is a reasonably deep well for the reaction with no activation barrier. A 38-kcal O_3S-O bond would fulfill this requirement. The fate of SO_4 is somewhat mysterious in this system as it does not lead to $SO_2 + O_2$. In fact, at much higher temperatures $O + SO_3 \rightarrow SO_2 + O_2$ appears to be a slow reaction[50,51] with appreciable activation energy. One would expect from its manner of formation from

$O + SO_3$ that the stable form of biradical SO_4 would be the triplet state and this could account for its dynamic stability relative to cyclic peroxy-SO_4.

One fate we might anticipate for radical SO_4 is self-polymerization to $(SO_4)_n$ either linear or cyclic or polymerization with SO_3 to form linear or cyclic $(SO_3)_nSO_4$ with a peroxide linkage. The polymer $(SO_4)_n$ could be looked upon as a copolymer of SO_2 and O_2, and we can estimate its $\Delta H_f°$ from known groups as -95 kcal/mol SO_4. Thus it would be stable by about 24 kcal/mol against decomposition into $SO_2 + O_2$ and it would be thermoneutral with respect to the depolymerization into $SO_3 + \frac{1}{2}O_2$. The O–O bond in such a polymer is estimated to be 22 kcal/mol, like that in $H_2S_2O_8$ so it could unzip at about room temperature.

The copolymer with SO_3 is expected to be more stable with an 11 kcal bond energy for the process

$$SO_4 + SO_3 \rightleftarrows \dot{O}(SO_2)O(SO_2)\dot{O}$$

While this is not enough to render the gas-phase dimer stable at 300 K, it could readily stabilize by sorbing on glass surfaces, or by forming there in a heterogeneous reaction.

It has been reported[52] that when an electric discharge is passed through a SO_2/O_2 mixture at 0.5 Torr ($O_2 \gg SO_2$) a white solid can be condensed with formula SO_4 and a melting point of +3 °C. On melting it evolves O_2 and leaves a liquid residue with the composition S_2O_7. These substances could well be the polymers discussed above which would be more stable in condensed states.

V. Oxidation of Sulfur-Containing Molecules

The kinetics of oxidation of sulfur compounds may be divided into two categories, the oxidation at low temperatures (~25 °C) which is of interest in photochemical smog formation and stratospheric chemistry and the high-temperature oxidation which is of interest in fossil fuel burning plants and smelters. There has been at least one very recent review in each of these two regimes which summarizes current thinking and evidence on reaction steps, and so we shall not attempt to repeat the discussions to be found there.[2,53] There is in addition a recent critical update of some of the elementary gas-phase reaction rate constants involving simple S-containing radicals with O, H, and other simple molecules and radicals in flames.[54] An additional article of interest in examining low-temperature oxidation processes and their relation to aerosol formation has also appeared recently.[55] Our discussion here will be confined to considering some of the critical elementary steps in these oxidation schemes and we shall start with the low-temperature photochemical system.

Photochemical smog formation refers to the oxidation of hydrocarbons present in ambient atmosphere at low concentration (1–10 ppm) triggered by photochemical (sunlight) decomposition of NO_2 also present in low concentrations (0.1–2.0 ppm). The process is accompanied by a catalytic production of O_3 (0.1 to 0.5 ppm maximum) and other oxidized species and usually aerosols.

Although photolysis produces O atoms from both NO_2 and O_3, these are rapidly scavenged by O_2 molecules in a rapid process and rapidly achieve a very low photostationary concentration dominated by:

$$NO_2 + h\nu\ (\lambda \leqslant 4100\ \text{Å}) \xrightarrow{1} NO + O$$

$$O + O_2 + M \xrightarrow{2} O_3 + M$$

$$NO + O_3 \xrightarrow{3} NO_2 + O_2$$

$$(O)_{ss} = (I_0\bar{\epsilon}_{NO_2})(NO_2)/k_2(O_2)(M)$$

I_0 is the flux of radiation and $\bar{\epsilon}_{NO_2}$ the weighted extinction coefficient of NO_2. Because of the low concentrations achieved, (~10^5–10^6 atoms/cm^3 at noon) reactions of O atoms with ambient molecules will not be of interest unless their bimolecular rate constants exceed 10^8 L/mol·s. Instead it appears that other radicals such as OH, HO_2, and RO_2 which react only very slowly or not at all with O_2 will dominate the reaction chemistry. Saturated hydrocarbons, for example, appear only to be attacked at significant rates by OH radicals.

The most important sulfur-containing species in ambient atmosphere is SO_2 and secondarily SO_3. Both of these react with O atoms at rates whose apparent bimolecular rate constants of about 10^8 L/mol·s[49,54] are close to the minimum rate considered significant. In very bright sunlight at higher NO_2 concentrations these reactions might be important, but not otherwise.

The reaction of OH with both SO_2 and SO_3 is expected to be extremely rapid with rate constants approaching 10^{11} and 10^{12} L^2/mol^2·s:

$$OH + SO_2 + M \rightarrow HOSO_2 + M$$

$$OH + SO_3 + M \rightarrow HOSO_3 + M$$

The resulting radicals have $DH°(HO{-}SO_2) = 36 \pm 3$ kcal and $DH°(HO{-}SO_3) = 39 \pm 2$ kcal and thus are expected to be quite stable with respect to dissociation. The addition reactions are expected to have negative temperature coefficients.

The HSO_4 radical can form a very strong OH bond (104 kcal) and is expected to be more active than RO radicals in either adding to double bonds of olefins or in abstracting H atoms from hydrocarbons. It can also react with NO to form mononitrosyl sulfuric acid $HO(SO_2)ONO$ with $DH°(HOSO_2O{-}NO) = 22 \pm 2$ kcal and $DH°(HOSO_2{-}ONO) = 36 \pm 2$ kcal. This addition reaction is expected to have very little or zero activation energy. The nitrosyl sulfuric acid has a very large heat of condensation, will be readily sorbed on surfaces, and exothermically hydrolyzed to sulfuric plus nitrous acids. It should also form metastable complexes with H_2O in the gas phase if the humidity is high enough.

HSO_4 will also react rapidly with NO_2 at almost every collision ($k \sim 10^{10}$ L/mol·s) to form nitryl sulfuric acid $HO(SO_2)ONO_2$. This species has an estimated $\Delta H_f°{}_{298} = -139 \pm 3$ kcal and about the same bond energy for redissociation as the nitrosyl ester, namely 22 ± 2 kcal. It will also form complexes with H_2O in the gas phase and hydrolyze readily on surfaces to $H_2SO_4 + HNO_3$.

Nitryl and nitrosyl sulfuric acid have relatively weak O–N bonds as estimated and at STP will have half-lives of about 1–10 s. At lower temperatures typical of the stratosphere (220 K) thermal dissociation is negligible while on hot, smoggy days redissociation is very fast.

It has been suggested that HSO_4 can react with O_2 to form the peroxy radical $HO(SO_2)O_3\cdot$ which can then go on to react with NO to form NO_2 and HSO_5.[56] Starting with our estimated $\Delta H_f°[HO(SO_2)O_3H] = -152 \pm 2$ we can estimate from group additivity rules for polyoxy compounds that $\Delta H_f°[HO(SO_2)O_3H] = -133 \pm 3$ kcal and $\Delta H_f°[HO(SO_2)O_4H] = -114 \pm 3$ kcal. In such polyoxides the $RO_{n+2}{-}H$ bond strength appears to be 90 ± 1 kcal as in H_2O_2 so that we can estimate $\Delta H_f°[HO(SO_2){-}O_3\cdot] = -95 \pm 3$ kcal. Thus the addition of O_2 to HSO_4 is endothermic by 20 ± 3.5 kcal and $HSO_6\cdot$ is not expected to exist. In contrast the radical $HOSO_2$ can form a bond with O_2 with a dissociation energy of about 16 ± 5 kcal and hence the radical HSO_5 is expected to be a significant species in smoggy atmosphere containing SO_2. $DH°(HOSO_3{-}O)$ is estimated to be 48 ± 5 kcal so that this radical should be capable of oxidizing NO to NO_2. Note that the adduct with NO or NO_2 will not be stable. The reaction $HSO_5 + NO_2 \rightleftarrows NO_3 + HSO_4$ is estimated to have $\Delta H° = 0 \pm 4$ kcal.

If we employ our rule that the reorganization energy of SO_2

TABLE XIV. H_f° **for Some Acid Anhydrides and Their Heats of Hydrolysis in the Ideal Gas State**

Ref	Anhydride	ΔH_f°	ΔH_{hyd}°
4	$(CH_3CO)_2O$	−137.1	−11.7
6	$(NO_2)_2O$	2.7	−9.1
(Table X)	$(HOSO_2)_2O$	−282 ± 3	−14 ± 3
7	Cl_2O	21.0	−1 ± 5
(Table X)	$HOSO_2F$	−180	−4
(Table X)	$HOSO_2Cl$	−133	−8
(4)	CH_3COF	−104	−6
(4)	CH_3COCl	−58.9	−8.5
(4)	CH_3COBr	−45.6	−8.6
(4)	CH_3COI	−30.3	−8.9
(Table X)	SO_2F_2	−181 ± 2	−5.7 ± 2
(Table X)	SO_2Cl_2	−84.8	−12.4
Table I	HCOSH	−30	−7.5 ± 1
4	$HCONH_2$	−44.5	1 ± 2
4	O_2NOMe	−28.6	6.4
4	ONOMe	−15.6	7.1
15	CH_3COOMe	−98.0	4.5
4	Me_2O	−44.0	6.0
39	HOOOH	−13	7.0
Table X	$HOSO_2(OMe)$	−170.5 ± 2	4.0

is 51 kcal then we can calculate $\Delta H_f^\circ(HO_2{-}SO_2) = -73 \pm 4$ kcal. This suggests that the radicals HO_2 (and RO_2) may react with SO_2 to form SO_3 + HO (and RO), respectively, with little or no activation energy. Thus SO_2 can, like NO, act as a catalyst for the conversion of relatively inert peroxy radicals into more active oxy radicals.

$$SO_2 + RO_2 \rightarrow SO_3 + RO$$

The intermediate adduct, RO_2SO_2, has a relatively weak $RO{-}OSO_2$ bond, 4 ± 4 kcal, and will not be stable.

The HSO_3 radical has a fairly strong $HSO_2{-}O$ bond which we estimate at about 97 ± 4 kcal; hence it will not oxidize NO_2, NO, or SO_2. We also calculate that it will not have any affinity for NO. However, it should react readily with NO_2 to form the fairly stable nitrosyl sulfuric acid:

$$NO_2 + HSO_3 \rightarrow HO({-}SO_2{-})ONO + 37 \pm 5\ \text{kcal}$$

As we have noted this will have a relatively short half-life at 300 K to dissociate into HSO_4 + NO or to hydrolyze.

The oxidation of sulfur compounds in flames and at high temperatures involves all possible valence states. Hence, isomeric forms of these species particularly as radicals become of interest. A very important reaction involves the interactions of H atoms with SO_2 and SO_3. $DH^\circ(SO_3{-}H) = 55 \pm 3$ kcal so that one expects H atoms to add very rapidly to SO_3. In high-temperature regimes the adduct is expected to have a very short lifetime for redissociation into SO_2 + OH for which $DH^\circ = 36$ so that the reaction

$$H + SO_3 \rightleftarrows HOSO_2^* \rightarrow HO + SO_2$$

is expected to proceed very rapidly with little or no activation energy.

The reactions of H atoms with SO_2 are probably more interesting in most flame systems. These reactions are complicated by the existence of isomeric forms of radicals and molecules. The compound H_2SO_2 has three isomeric forms $(HO)_2S$, HSO(OH), and H_2SO_2. For these forms we have estimated ΔH_f° of −67 ± 5, −72 ± 5, and −64 ± 4, respectively. The radical HSO_2 has two isomeric forms $H{-}SO_2$ and $HO{-}S{=}O$ for which by our various rules we can deduce ΔH_f° of −42 ± 4 and −60 ± 3 kcal, respectively. Thus the latter will be significantly more stable with an H-OSO bond dissociation energy of 41 kcal. Efforts to measure the rate of addition of H atoms to SO_2 in flow systems have been made difficult by the very rapid wall recombination.[57] However, flame studies which have been recently reviewed[54] indicate a fairly rapid three-body reversible recombination above 1600 K. This would be compatible with the 41-kcal bond energy.

Sulfur compounds in the divalent state will be expected to react very rapidly with O atoms to form sulfoxides:

$$R_2S + O \rightarrow R_2SO$$

This reaction is very exothermic (Table VIII) and in the gas phase can be followed by dissociation of the weaker R-S bond. Gutman and coworkers[58] have shown that these reactions at room temperatures proceed with zero activation energy for RSH and R_2S and have suggested that with H_2S the excited adduct H_2SO^* can rearrange to give the isomeric HOSH* which is estimated to be about 20 ± 5 kcal more stable. With the internal energies available in these adducts this seems entirely reasonable.

One of the other high-temperature reactions which has excited some interest has been the bimolecular reaction between NO_2 and SO_2:

$$NO_2 + SO_2 \rightarrow NO + SO_3 + 11\ \text{kcal}$$

Despite its exothermicity this reaction appears to have a surprisingly high activation energy of the order of 26 kcal.[59] Rate studies on this system have proven difficult because the bimolecular reaction of $2NO_2 \rightarrow 2NO + O_2$ is faster than the competing reactions. In examining this reaction one notices that the transition state must be close in structure to the radical species:

$$O{=}N{-}O{-}SO_2$$

We can estimate the ΔH_f° for this species by observing that $\Delta H_f^\circ(ONOSO_3H) = -125 \pm 3$ kcal. If the S-OH bond dissociation energy in this anhydride is the same as its value in H_2SO_4 (Table III), then we can calculate $\Delta H_f^\circ(ONO{-}SO_2) = -46 \pm 4$ kcal. Thus the radical lies above $SO_2 + NO_2$ by 17 ± 4 kcal and this would be a minimum activation energy for the reaction. On this basis the transition state for the reaction lies between the free molecules and the above radical with an intrinsic energy only 9 kcal above the radical. This 9 kcal would be a reasonable intrinsic activation energy for an atom-transfer reaction. A similar situation occurs in the reaction of NO_2 with CO which is exothermic to form NO + CO_2 by 54 kcal but has an activation energy of 27 kcal. By similar methods we can estimate $\Delta H_f^\circ(O{-}NOCO) = 1 \pm 3$ kcal so that the radical lies 19.5 ± 3 kcal above NO_2 + CO in ΔH_f° and the transfer reaction has an intrinsic activation energy of only 8 kcal.

VI. Appendix: Methods of Estimation of ΔH_f° of Acid Anhydrides

To estimate the ΔH_f° of the various sulfur and nitrogen oxyacid anhydrides we have made use of the analogies which represent a correction to the rules of bond additivity. Data exist for a number of acid anhydrides and for the corresponding acids. These are summarized in Table XIV where we list in addition data on the heats of hydrolysis of these anhydrides in the ideal gas state. The listings are roughly in order of exothermicity and we notice that they range from $\Delta H = -14$ to +6.0 kcal. The range is not random but appears to be correlated with the acidity (pK_a) of the two acids involved. Thus anhydrides of acids whose $pK_a \leqslant 5$ seem to hydrolyze with $\Delta H_{hyd} \approx -10 \pm 2$ kcal. As the pK_a of one or more of the acids decreases, this changes to positive. Anhydrides of MeOH, for example, seem to have $\Delta H_{hyd} \sim 5 \pm 2$ kcal.

On the basis of the above correlations we would expect that anhydrides of nitric and sulfuric and acetic acids in any combination would have $\Delta H_{hyd} = -12 \pm 2$ kcal. And on this basis we would estimate:

$$\Delta H_f^\circ[HO(SO_2)O\ COCH_3] = -212 \pm 2$$

$$\Delta H_f^\circ[\mathrm{HO(SO_2)ONO_2}] = -139 \pm 2$$

$$\Delta H_f^\circ[\mathrm{CH_3(CO)ONO_2}] = -65 \pm 2$$

On the same basis we would estimate:

$$\Delta H_f^\circ[\mathrm{O_2N{-}NH_2}] = 15 \pm 2$$

$$\Delta H_f^\circ[\mathrm{HO(SO_2)NH_2}] = -124 \pm 2$$

For HONO we can bracket the anhydride ΔH_f° between that of stable N_2O_3 (+19.8 kcal) and separated NO + NO_2 (+29.4 kcal). A reasonable choice would be $\Delta H_f^\circ[(\mathrm{ON})_2\mathrm{O}] = 24 \pm 2$ kcal. Bond additivity would then yield $\Delta H_f^\circ(\mathrm{ONONO_2}) = 13.5 \pm 1$ kcal which can be compared to 2.5 kcal for the stable forms of N_2O_4. $\Delta H_{\mathrm{hyd}}^\circ[(\mathrm{ON})_2\mathrm{O}]$ is then −2.5 kcal while $\Delta H_{\mathrm{hyd}}^\circ[\mathrm{ONONO_2}] = -6$ kcal, both of which seem quite reasonable. On this basis, guided by the pK_a considerations, we would estimate:

$$\Delta H_f^\circ[\mathrm{HO(SO_2)ONO}] = -129 \pm 2\ \mathrm{kcal}$$

$$\Delta H_f^\circ[\mathrm{CH_3(CO)ONO}] = -56 \pm 2\ \mathrm{kcal}$$

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VII. References and Notes

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