

# Thermochemistry and Kinetics of Sulfur-Containing Molecules and Radicals

SIDNEY W. BENSON

Department of Chemistry, University of Southern California, Los Angeles, California 90007

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## 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.<sup>1</sup> 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.<sup>2</sup> 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.<sup>3</sup>

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<sup>4</sup> and by Stull, Westrum, and Sinke.<sup>5</sup> Perhaps the most detailed and critical evaluation on selected compounds comes from the JANAF series.<sup>6</sup> The NBS series of "Selected Values of Chemical Thermodynamic Prop-

erties", Technical Note 270-3,<sup>7</sup> 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,<sup>8</sup> and we shall borrow heavily from this particularly for data on  $S^\circ$  and  $C_p^\circ$  and the methodology of group additivity.

Much less information exists on the heats of formation of sulfur-containing radicals. Mackle<sup>9</sup> made the first extensive survey of bond strengths in organic sulfur molecules, and some of these were included by Kerr<sup>10</sup> 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.<sup>11</sup> Some of this has been in turn updated in a recent review.<sup>12</sup> 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  $C_p^\circ$  and  $S^\circ$  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.<sup>15</sup> 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.<sup>4,5,8</sup> 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<sup>8</sup> 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

TABLE I.  $\Delta H_f^\circ$  and  $S^\circ$  of Some Molecules and Radicals of Divalent Sulfur<sup>a,b</sup>

Ref	Species	$\Delta H_f^\circ$ 298	(E strain) <sup>b</sup>	$S^\circ$ 298
6	S	66.3		40.1
6	S <sub>2</sub>	30.7		54.5
19	c-S <sub>3</sub>	32.5 ± 1	(22.9)	63 ± 1.5
19	c-S <sub>4</sub>	31 ± 2	(18.4)	72 ± 2
7, 19	c-S <sub>6</sub>	24.5	(5.3)	84.9
7	c-S <sub>8</sub>	24.5	(-1.1)	103.0
6	SH	35 ± 1		46.7
7	H <sub>2</sub> S	-4.9		49.2
	HS <sub>2</sub>	[22.1 ± 1]		[61.4]
13a, 7	H <sub>2</sub> S <sub>2</sub>	3.8		62.3
	HS <sub>3</sub>	[25.3 ± 1]		[74.8]
13a	H <sub>2</sub> S <sub>3</sub>	7.4		[75.7]
13a	H <sub>2</sub> S <sub>4</sub>	10.6		[89.1]
6	SO	1.2		53.0
	SOH	[5 ± 4]		[57 ± 1]
	S(OH) <sub>2</sub>	[-67 ± 4]		[70 ± 1]
6	SF	3 ± 2		53.8
6	SF <sub>2</sub>	-71 ± 3		61.6
	SCI	[36.5 ± 2]		57.3
7	SCl <sub>2</sub>	-4.7		67.2
	SBr <sub>2</sub>	[5 ± 4]		
6	FSSF	-80 ± 10		70.3
5	S <sub>2</sub> Cl <sub>2</sub>	-4.7		76.4
7	S <sub>2</sub> Br <sub>2</sub> (l)	-3		
	S <sub>2</sub> Br <sub>2</sub> (g)	[+9]		
48	SN	68 ± 5		53.1
28, 6	SC	64.8; 67 ± 6		50.3
6	CS <sub>2</sub>	28.0		56.8
6	CSO	-33.1		55.3
26	CH <sub>2</sub> =S	24.3		[56 ± 1]
14	CH <sub>3</sub> S	34.2 ± 1.5		57.6
4	CH <sub>3</sub> SH	-5.4		61.0
	CH <sub>2</sub> =CHSH	[21.0 ± 2]		[67 ± 1]
	CH <sub>2</sub> =CHS·	[53 ± 3]		[62.0]
4	CH <sub>3</sub> SCH <sub>3</sub>	-8.9		68.3
7	C <sub>2</sub> H <sub>5</sub> SH	-11.0		70.8
14	C <sub>6</sub> H <sub>5</sub> S	56.8 ± 1.5		76.5
4	C <sub>6</sub> H <sub>5</sub> SH	26.7		80.5
7	c-CH <sub>2</sub> CH <sub>2</sub> S	19.7	(19.5)	61.0
4	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SH	22.9		[91.0]
4	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	55.3		
	CH <sub>2</sub> (SH) <sub>2</sub>	[8 ± 2]		
	CH <sub>3</sub> S <sub>2</sub>	[17.3 ± 1]		
7	CH <sub>3</sub> SSCH <sub>3</sub>	-5.8		80.5
4	C <sub>6</sub> H <sub>5</sub> SSC <sub>6</sub> H <sub>5</sub>	58.4		
	CH <sub>3</sub> SSS	[20.5 ± 1]		
	CH <sub>3</sub> S <sub>4</sub> CH <sub>3</sub>	[0.4 ± 1]		
4	CH <sub>3</sub> COSH	-43 ± 1		74.9
	HCOSH	[-30 ± 1]		
	(CH <sub>3</sub> O) <sub>2</sub> S	[-59 ± 5]		
	CH <sub>3</sub> SCI	[-6.8 ± 1.5]		
	CH <sub>3</sub> SSCI	[-5.1 ± 1.5]		
	C <sub>6</sub> H <sub>5</sub> SCI	[25.3 ± 1.5]		
	C <sub>6</sub> H <sub>5</sub> S <sub>2</sub> Cl	[27 ± 1.5]		
8	(NH <sub>2</sub> ) <sub>2</sub> C=S	-6.0		72.4
7	HNC=S	30.0		59.2
7	CH <sub>3</sub> NC=S	31.3		69.3
7	CH <sub>3</sub> SCN	38.3		[69 ± 1]
4	[(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NS] <sub>2</sub>	-16.5 ± 1.5		
4	(CNS) <sub>2</sub>	82.3		

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

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

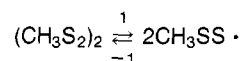
The group values which we shall use to estimate the thermochemistry of compounds not given here have been recently

republished,<sup>15</sup> but some corrections based on recent studies are in order. The changes are as follows.

For the S-(C)(C<sub>d</sub>) group we shall use the value  $\Delta H_f^\circ$  298 = 13.0 kcal instead of the original 10.0 kcal. For the related group S-(H)(C<sub>d</sub>) based on various analogies we derive the value  $\Delta H_f^\circ$  298 = 6.1 kcal. For the S-(S)<sub>2</sub> group we use  $\Delta H_f^\circ$  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<sub>d</sub>)<sub>2</sub>. If we assign  $\Delta H_f^\circ$  for the latter as  $\Delta H_f^\circ$  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  $\Delta H_f^\circ$  298 and  $S^\circ$  298 for key divalent molecules and related radicals containing sulfur. The values of  $\Delta H_f^\circ$  for S, S<sub>2</sub>, 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<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SH, CH<sub>3</sub>SH, and C<sub>2</sub>H<sub>5</sub>SH<sup>11</sup> and for once is in good agreement with data on electron impact. Of these three kinetic studies the first on C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SH 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<sup>15</sup> s<sup>-1</sup> and an assignment of the scaled activation energy to the  $\Delta E$  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  $\Delta H_f^\circ$  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  $\Delta H_f^\circ$  for CH<sub>3</sub>S and C<sub>6</sub>H<sub>5</sub>S listed here and those in earlier reviews. The values listed here are from recent studies using VLPP techniques<sup>14</sup> which yield high-pressure kinetic parameters in excellent agreement with values of the absolute values of the rate constants from earlier studies<sup>11</sup> which employed the toluene carrier technique. The assignment of the observed, "scaled" activation energy to  $\Delta E_T$  for the overall fission at reaction temperature together with a correction of  $\Delta H_T$  to room temperature  $\Delta H_{298}$  based on an estimated  $\Delta C_p$  lead to a change from earlier values of about 4 kcal. It would be difficult to justify a change in the  $\Delta H_f^\circ$  298 for these radicals by more than the indicated uncertainties.

Kende et al.<sup>16</sup> have measured the rates of fission of (CH<sub>3</sub>S<sub>2</sub>)<sub>2</sub> in toluene at 65 °C using a radical scavenger to follow the first-order reaction.



They reported  $kf = 5 \times 10^{17-36.6/\theta} \text{ s}^{-1}$  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<sup>2</sup> and since their temperature range was very limited (30 °C) we scale the Arrhenius parameters to  $A = 5 \times 10^{15} \text{ s}^{-1}$  (comparable to peroxide fissions) and  $E = 33.6 \text{ kcal/mol}$ . 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.<sup>17</sup> 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<sup>15</sup> to deduce a value for  $\Delta H_f^\circ$  298(MeS<sub>4</sub>Me) = 0.4 kcal/mol we deduce the value of  $\Delta H_f^\circ$  298(CH<sub>3</sub>SS·) = 17.3 ± 1 kcal/mol shown in Table I. This value together with group additivity yields the value  $\Delta H_f^\circ$  298(HSS·) = 22.1 ± 1 kcal/mol (Table I) and the values also shown in Table I for HS<sub>3</sub>· and CH<sub>3</sub>S<sub>3</sub>·.

TABLE II. Effect of Polarity and Electronegativity on Differences in Heat of Formation between Hydrogen (HX) and Methyl Derivative (CH<sub>3</sub>X)<sup>a</sup>

X	$\Delta H_f^\circ(\text{HX})$	$\Delta H_f^\circ(\text{CH}_3\text{X})$	$\Delta(\Delta H_f^\circ)$	X	$\Delta H_f^\circ(\text{HX})$	$\Delta H_f^\circ(\text{CH}_3\text{X})$	$\Delta(\Delta H_f^\circ)$
F	-64.8	-55 ± 2	-9.8 ± 2	I	6.3	3.3	3.0
OH	-57.8	-48.0	-9.8	SCH <sub>3</sub>	-5.4	-8.9	3.5
O(SO <sub>3</sub> )CH <sub>3</sub>	-170.5	-164	-6.5	C <sub>2</sub> H <sub>5</sub>	-20.2	-24.8	4.6
O(CO)CH <sub>3</sub>	-103.8	-98	-5.8	S <sub>2</sub> H	3.8	-1.0	4.8
NH <sub>2</sub>	-11.0	-5.5	-5.5	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	-24.8	-30.2	5.4
OCH <sub>3</sub>	-48.0	-44.0	-4.0	C <sub>2</sub> H <sub>3</sub>	12.5	4.9	7.6
ONO <sub>2</sub>	-32.1	-28.6	-3.5	C <sub>6</sub> H <sub>5</sub>	19.8	12.0	7.8
ONO	-18.3	-15.6	-2.7	NO	23.8	16	8
Cl	-22.0	-19.6	-2.4	COCH <sub>3</sub>	-39.7	-51.7	12.0
O <sub>2</sub> H	-32.6	-31.3	-1.3	CN	32.3	[19 ± 2]	13 ± 2
NH(CH <sub>3</sub> )	-5.5	-4.5	-1.0	COOH	-90.5	-103.8	13.3
Br	-8.7	-9.5	0.8	CF <sub>3</sub>	-167	-178	11
SH	-4.8	-5.4	0.6	SiH <sub>3</sub>	8	-4	12
N(CH <sub>3</sub> ) <sub>2</sub>	-4.5	-5.9	1.4	SnH <sub>3</sub>	39	[28 ± 3]	11 ± 3
CH <sub>3</sub>	-17.9	-20.2	2.3				

<sup>a</sup> 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.<sup>18</sup> Note that we have used a slightly different value for the S-(S)<sub>2</sub> group than that listed in ref 15, namely  $\Delta H_f^\circ_{298}(\text{S-S}_2) = 3.2$  kcal/mol. This is based on the  $\Delta H_f^\circ$  data for the sulfanes<sup>13a,b</sup> which indicate a very consistent value for this group up to H<sub>2</sub>S<sub>6</sub>. This value for the S-(S)<sub>2</sub> group together with the observed value for c-S<sub>3</sub> (Table I) leads to a value of 22.9 kcal for the strain energy in the S<sub>3</sub> ring. This is comparable to values of 17.7 to 21 reported for the various ethylene sulfides.<sup>8</sup> Using this new group value we find strain energies of 5.3 kcal in the c-S<sub>6</sub> ring and -1.1 kcal in the c-S<sub>8</sub> 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<sub>2</sub>S are 0.82 and 0.97 D, respectively,<sup>20</sup> while the H-Br and H-S bond lengths are 1.415 and 1.345 Å, respectively.<sup>21</sup> CH<sub>3</sub>Br and CH<sub>3</sub>SH have similar dipole moments of 1.81 and 1.52 D, respectively,<sup>20</sup> the C-S and C-Br bond lengths in these compounds are 1.82 and 1.93 Å, respectively,<sup>21</sup> 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  $\Delta H_f^\circ$  for the compounds HX and CH<sub>3</sub>X.

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<sub>3</sub> and CF<sub>3</sub>. Similarly, while CH<sub>3</sub> for H substitution in HOH makes  $\Delta H_f^\circ$  more positive by 9.8 kcal, a second CH<sub>3</sub>/H substitution increases  $\Delta H_f^\circ$  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<sup>22-25</sup> and hence its polarity.

As the polarity of the central atom goes from very negative to very positive values the CH<sub>3</sub>/H substitution covers a range of from -10 to +14 kcal/mol. Such a relation permits us to estimate  $\Delta H_f^\circ$  for compounds with uncertainties of about ±2 kcal/mol. Thus we can estimate for the unknown H-NO<sub>2</sub> 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  $\Delta H_f^\circ$  for CH<sub>2</sub>(SH)<sub>2</sub> from the value of CH<sub>2</sub>Br<sub>2</sub> as  $6 \pm 2$  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<sub>3</sub>, 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  $\Delta H_f^\circ$  from R-Br compounds by  $4.0 \pm 0.3$  kcal. This is true for R = H, CH<sub>3</sub>, and C<sub>2</sub>H<sub>5</sub> (Table II) and appears to be true for R-C<sub>2</sub>H<sub>3</sub> 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  $\Delta H_f^\circ$  of phenyl compounds differ only by 1.7 kcal since vinyl and phenyl have about the same kind of carbon atoms.<sup>23</sup> 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  $2.6 \pm 1.5$  kcal lower than  $\Delta H_f^\circ(\text{CH}_3\text{COSH})$  which is well within the expectations of our Br/S<sub>H</sub> substitution rule.

Using the H/CH<sub>3</sub> substitution value observed for HCOOH and CH<sub>3</sub>COOH (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<sup>27</sup> was the weakness of the single bonds between the isoelectronic groups NH<sub>2</sub>, OH, and F. These are among the weakest single bonds in the periodic table and decrease uniformly in the sequence CH<sub>3</sub>-CH<sub>3</sub> (88), NH<sub>2</sub>-NH<sub>2</sub> (70), HO-OH (50), F-F (38). There is a comparable decrease in bond strengths in the related sequence in the second-row SiH<sub>3</sub>-SiH<sub>3</sub>, PH<sub>2</sub>-PH<sub>2</sub>, 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  $\sigma$  and  $\pi$  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<sub>2</sub> is some 17 kcal weaker than the O-O bond in O<sub>2</sub>. 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 <sub>2</sub>	102.5	O <sub>2</sub>	119.2
SO	124.7	OS	124.7
SC=S	103.4	SC=O	157.5
CH <sub>2</sub> =S	129 ± 5	CH <sub>2</sub> =O	172 ± 3
OC=S	73.3	OC=O	127.2
C=S	173	C=O	257
CH <sub>3</sub> NC=S	71	CH <sub>3</sub> NC=O	[133 ± 4]

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

RS-H <sup>a</sup>	Bond dissociation energy	RS-H <sup>a</sup>	Bond dissociation energy
·S-H	83.6 ± 1	HS <sub>2</sub> -H	70 ± 1.5
HS-H	92.0 ± 1	Alk-S <sub>2</sub> -H	70 ± 1.5
CH <sub>3</sub> S-H	92 ± 1.5	HS <sub>3</sub> -H	70 ± 1.5
C <sub>2</sub> H <sub>5</sub> S-H	92 ± 2	HS <sub>3+n</sub> -H	70 ± 1.5
Alk-S-H	92 ± 2	Alk-S <sub>3+n</sub> -H	70 ± 1.5
C <sub>6</sub> H <sub>5</sub> S-H	82 ± 1.5		
·S <sub>2</sub> -H	60.5 ± 1.5		
CH <sub>2</sub> =CHS-H	[84 ± 2]		

<sup>a</sup> 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<sub>2</sub>O and CH<sub>2</sub>S 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<sub>2</sub>O with CO<sub>2</sub>. The 45 kcal apparent smaller OC=O bond strength in the latter compound can be associated with the extra  $\pi$  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<sub>2</sub>=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<sub>2</sub>, COS, CS<sub>2</sub> there is a constant 61 kcal change in  $\Delta H_f^\circ$  on replacing O by S. This difference is maintained in the related pair of very polar compounds CO(NH<sub>2</sub>)<sub>2</sub> and CS(NH<sub>2</sub>)<sub>2</sub> for which data exist in aqueous solutions<sup>7</sup> and suggests that it should be the same in the paired compounds CH<sub>3</sub>NCO/CH<sub>3</sub>NCS and HNCO/HNCS. On this basis we would assign  $\Delta H_f^\circ_{298}[\text{HNCO}(\text{g})] = -30$  kcal. This would make it about 6 ± 2 kcal/mole more stable than the isomeric HOCN.<sup>7</sup>

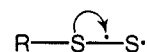
In Table IV we list some S-H bond dissociation energies derived from the data on  $\Delta H_f^\circ$  shown in Table I and the known  $\Delta H_f^\circ$  of H and other free radicals (ref 15). A number of features are noteworthy. In the saturated monosulfur compounds RS-H the S-H bond is 92 kcal, independent 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<sub>2</sub> and O reflecting a delocalization of the ring electrons and charge donation to the radical center. The effect in C<sub>6</sub>H<sub>5</sub>S· measured against saturated RS· radicals is seen to be 10 kcal, significantly lower than the 13.5 kcal observed in C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>· and the 17 kcal found in C<sub>6</sub>H<sub>5</sub>O·.<sup>29</sup> As we shall see, this is a reflection of the weaker  $\pi$  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 <sub>3</sub>	66 ± 1.5	CH <sub>3</sub> S-CH <sub>3</sub>	77 ± 1.5
·S-C <sub>2</sub> H <sub>5</sub>	63 ± 2	Alk-S-CH <sub>3</sub>	77 ± 1.5
·S-Alk	63 ± 2	C <sub>6</sub> H <sub>5</sub> S-CH <sub>3</sub>	67.4 ± 1.5
·S-C <sub>6</sub> H <sub>5</sub>	88.5 ± 1.5	CH <sub>3</sub> S-C <sub>2</sub> H <sub>5</sub>	74 ± 1.5
		<i>n</i> -Alk-S-C <sub>2</sub> H <sub>5</sub>	74 ± 2
HS-CH <sub>3</sub>	75 ± 1.5		
HS-C <sub>2</sub> H <sub>5</sub>	72 ± 1.5	<i>n</i> -Alk-S- <i>i</i> Pr	73.5 ± 1.5
HS- <i>i</i> Pr	71 ± 1.5	<i>n</i> -Alk-S- <i>t</i> Bu	71 ± 1.5
HS- <i>t</i> Bu	69 ± 1.5	CH <sub>3</sub> S-C <sub>6</sub> H <sub>5</sub>	89.2 ± 2
HS-C <sub>2</sub> H <sub>3</sub>	83 ± 3	CH <sub>3</sub> S-CN	97 ± 1.5
HS-C <sub>6</sub> H <sub>5</sub>	86.5 ± 2		
HS-(CO)H	74 ± 2	HS <sub>2</sub> -CH <sub>3</sub>	57 ± 1.5
HS-COCH <sub>3</sub>	73 ± 2	Alk-S <sub>2</sub> -CH <sub>3</sub>	57 ± 1.5
·S <sub>2</sub> -CH <sub>3</sub>	47.5 ± 1.5	Alk-S <sub>2</sub> -C <sub>2</sub> H <sub>5</sub>	54 ± 1.5
·S <sub>2</sub> -C <sub>2</sub> H <sub>5</sub>	44.5 ± 1.5	Alk-S <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	69.5 ± 1.5
·S <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	60 ± 2	Alk-S <sub>n</sub> -C <sub>2</sub> H <sub>5</sub>	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<sub>2</sub>S<sub>*n*+1</sub> is some 22 kcal weaker than the other S-H bonds. This difference can be identified with the partial double or  $\pi$  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<sub>2</sub>O<sub>2</sub> where the effect relative to ROH is about 14 kcal.<sup>27</sup>

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  $\pi$  electrons exert a bond weakening effect comparable to their effect on S-H bonds. Of particular interest for the symmetrical compounds X<sub>2</sub>S 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<sub>2</sub>O 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  $\Delta H_f^\circ$  of the two sets of compounds R<sub>2</sub>O and R<sub>2</sub>S. We note from Table II that the substitution of CH<sub>3</sub> for H in H<sub>2</sub>O and CH<sub>3</sub>OH increases  $\Delta H_f^\circ$  while the opposite is the case for CH<sub>3</sub>/H substitution in H<sub>2</sub>S.

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  $\Delta H_f^\circ$  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<sub>2</sub>-Cl (Table VI). The heats of formation of these mixed compounds have been estimated by methods of bond additivity from  $\Delta H_f^\circ$  for SCl<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub>. 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<sub>2</sub>S<sub>2</sub> and H<sub>2</sub>S<sub>3</sub> (Table VI) we find a difference of only 16 ± 2.5 kcal with a similar value for the HS<sub>2</sub>-S<sub>2</sub>H/HS<sub>2</sub>-SH difference. These are real discrepancies and reflect the fact that H<sub>2</sub>S 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, signifi-

cantly 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  $9.5 \pm 1$  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  $\pi$  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  $\pi$  bond energy formed in the  $C_2H_4$  product.<sup>27</sup> It has been shown to be a transferable quantity independent of the groups R.<sup>30</sup> 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  $\pi$  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  $DH^\circ_1 - DH^\circ_2$  by double the amount of stabilization in the radical.

If we adopt the stabilization energy in  $RS_2\cdot$  as  $21 \pm 1$  kcal, then the  $\pi$  bond strength in  $S_2$  can be estimated as the nearly universal  $DH^\circ_1 - DH^\circ_2 = 9.5 \text{ kcal} + 2 \times 21 = 51.5 \pm 2$  kcal. A similar calculation for peroxides yields a value of  $71 \pm 1.5$  kcal for the  $\pi$  bond strength in  $O_2$ . This latter is very reasonable compared to  $\pi$  bond strengths observed in olefins ( $\sim 60$  kcal), acetylenes ( $\sim 72$  kcal), and aldehydes ( $\sim 76$  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  $133.5 \pm 3$  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  $133.5 \pm 3$  can then be taken as the  $\pi$  bond strength in  $CH_2S$ , namely,  $56.5 \pm 3$  kcal. This is very close to the value of the  $\pi$  bond strength in olefins and is consistent with the observation that  $\Delta H_f^\circ(CH_2=S)$  is very closely the average of  $\Delta H_f^\circ$  for  $S_2$  and  $C_2H_4$ . The average is 21.6 kcal/mol compared to the  $24 \pm 3$  reported (Table I).

The above value of the C=S  $\pi$  bond strength is only  $3 \pm 3$  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<sup>11</sup> as well as appreciable sensitivity to vessel wall condition and traces of oxygen. Compounds containing  $\pi$  bonds to sulfur are extremely susceptible to polymerization<sup>26,31</sup> 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<sup>32</sup> such as in the pyrolysis of episulfides which produce olefins plus sulfur.

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

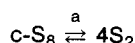


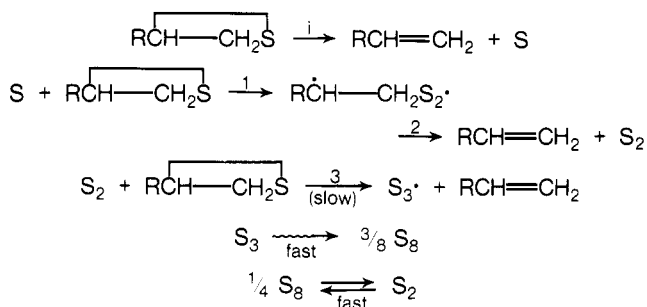
TABLE VI. Some S-S and Other Bond Dissociation Energies for Divalent Sulfur

RS-SR'	Bond dissociation energy	RS-X	Bond dissociation energy
HS-SH	66 ± 2	·S-F	82 ± 3
CH <sub>3</sub> S-SCH <sub>3</sub>	74 ± 2	FS-F	92 ± 3
Alk-S-S-Alk	74 ± 2	CH <sub>3</sub> S-Cl	[70 ± 3]
		CH <sub>3</sub> S <sub>2</sub> -Cl	[51 ± 2.5]
HS <sub>2</sub> -SH	50 ± 2	ClS <sub>2</sub> -Cl	[51 ± 2]
HS <sub>2</sub> -SCH <sub>3</sub>	54 ± 2	·S <sub>2</sub> -Cl	[42 ± 2]
HS <sub>2</sub> -S-Alk	54 ± 2	C <sub>6</sub> H <sub>5</sub> S-Cl	[31 ± 2.5]
HS <sub>2</sub> -SC <sub>6</sub> H <sub>5</sub>	44 ± 2	ClS-Cl	[70 ± 3]
		·S-Cl	[60 ± 2]
		BrS-Br	[62 ± 4]
HS <sub>2</sub> -S <sub>2</sub> H	33.6 ± 2	·S-Br	[52 ± 4]
Alk-S <sub>2</sub> -S <sub>2</sub> -Alk	33.6 ± 2	BrS <sub>2</sub> -Br	[42 ± 4]
RS <sub>2+n</sub> -S <sub>2+m</sub> R	33.6 ± 2	·S-OH	[70 ± 4]
		HOS-OH	[81 ± 4]
HS-S·	79 ± 1	C <sub>6</sub> H <sub>5</sub> N=N-SC <sub>6</sub> H <sub>5</sub>	[29 ± 1] <sup>62</sup>
CH <sub>3</sub> S-S·	83 ± 1	(Ar) <sub>3</sub> CS-NO	[25 ± 1] <sup>63</sup>
C <sub>6</sub> H <sub>5</sub> S-S·	74 ± 1.5	CH <sub>3</sub> S-NO	[25 ± 1]
FS-SF	61 ± 4		
C <sub>6</sub> H <sub>5</sub> S-SH	61 ± 1.5		
C <sub>6</sub> H <sub>5</sub> S-SCH <sub>3</sub>	65 ± 1.5		
C <sub>6</sub> H <sub>5</sub> S-SC <sub>6</sub> H <sub>5</sub>	55 ± 1.5		
RS <sub>2</sub> -S·	63 ± 1		
RS <sub>2</sub> -S <sub>2</sub> ·	47.5 ± 1		

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

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

Since  $(S_2)$  is proportional to  $(S_8)^{1/4}$ , a fourfold change in  $(S_8)$  gives only a 40% change in  $(S_2)$ .  $\Delta H_a = 24.7$  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:

$$-d(\text{RC}_2\text{H}_3\text{S})/dt = k_1(\text{RC}_2\text{H}_3\text{S}) + k_3K_a^{1/4}(S_8)^{1/4}(\text{RC}_2\text{H}_3\text{S})$$

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  $\text{R}-\dot{\text{C}}\text{H}-\text{CH}_2\text{S}_3\cdot$  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	$\Delta H_f^\circ_{298}$	$S^\circ_{298}$	Ref	Species	$\Delta H_f^\circ_{298}$	$S^\circ_{298}$
(6)	SO <sub>2</sub>	-70.9	59.3		SOH <sub>2</sub>	[-16 ± 4]	
(7)	SO <sub>2</sub> (aq)	-77.2	38.7	(4)	SO(Me) <sub>2</sub>	-36.0	73.2
(2, 6)	S <sub>2</sub> O	-10	63.8	(6)	SSF <sub>2</sub>	[<-60 ± 6]	70.0
(6)	SOF <sub>2</sub>	-130 ± 5	66.7			-96 ± 10	70.0
(7)	SOCl <sub>2</sub>	-51	74.0	(6)	SF <sub>3</sub>	-119 ± 4	66 ± 1.5
(7)	SOBr <sub>2</sub>	-21.8		(4)	SO(Et) <sub>2</sub>	-49.1	
(6)	SF <sub>4</sub>	-183 ± 5	71.6	(4)	SO(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	25.6	
(7)	SO(HO) <sub>2</sub> (aq)	-145.5	55.5	(4)	SO(NEt <sub>2</sub> ) <sub>2</sub>	-66.3	
	SO(HO) <sub>2</sub>	[-127 ± 3]	[69]		S=S(Me) <sub>2</sub>	[4 ± 3]	
(4)	SO(OMe) <sub>2</sub>	-115.5			S=SH <sub>2</sub>	[10 ± 7]	
(4)	SO(OEt) <sub>2</sub>	-131.9			CH <sub>2</sub> SO	[-12 ± 5]	
60	C <sub>6</sub> H <sub>5</sub> S(SO)C <sub>6</sub> H <sub>5</sub>	[34 ± 2]			HOSO(O <sub>2</sub> H)	[-105 ± 5]	
60, 64	C <sub>6</sub> H <sub>5</sub> SO	[13 ± 2]					
	(C <sub>6</sub> H <sub>5</sub> SO) <sub>2</sub>	[11 ± 4]					
(4)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SOC <sub>6</sub> H <sub>5</sub>	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 <sub>2</sub> S=O	[71 ± 4]
OS=O	132	Me <sub>2</sub> S=O	86.6
SS=O	100	Et <sub>2</sub> S=O	88.7
F <sub>2</sub> S=O	118 ± 6	CH <sub>2</sub> =S=O	[95 ± 5]
(HO) <sub>2</sub> S=O	[118 ± 6]	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S=O	89.3
(MeO) <sub>2</sub> S=O	[116 ± 6]		
Cl <sub>2</sub> S=O	105	OS=S	77
Br <sub>2</sub> S=O	[86 ± 4]	F <sub>2</sub> S=S	[>57 ± 8]
C <sub>6</sub> H <sub>5</sub> S=O	[103 ± 2]	Me <sub>2</sub> S=S	[53 ± 4]
C <sub>6</sub> H <sub>5</sub> SSOC <sub>6</sub> H <sub>5</sub>	[83 ± 4]	H <sub>2</sub> S=S	[51 ± 7]
C <sub>6</sub> H <sub>5</sub> SOSOC <sub>6</sub> H <sub>5</sub>	[83 ± 4]		

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

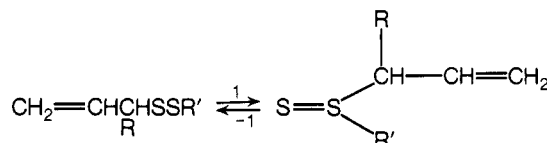
### III. Tetravalent Sulfur

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<sub>2</sub> in the tetravalent states or >SO<sub>2</sub>, >SOF<sub>2</sub>, and >SF<sub>4</sub> derivatives in the hexavalent states. As such they are strongly reminiscent 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<sub>2</sub>SO<sub>3</sub> in aqueous solution is better considered as the isomer H<sub>2</sub>O·SO<sub>2</sub>. Based on data for differences in  $\Delta H_f^\circ$  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<sub>2</sub>. Both of these compounds can be prepared, presumably pure.<sup>33</sup> However, if the liquid FSSF is allowed to warm up above 0 °C it spontaneously changes over to the more stable SSF<sub>2</sub>. In contrast dialkyl disulfides RSSR<sup>1</sup> 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<sup>34</sup> have convincingly demonstrated that allyl disulfides can undergo a Cope-type rearrangement with a thiosulfoxide intermediate



This intermediate can be trapped by P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> to give SP(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and R'SCHRCH=CH<sub>2</sub>. At high enough concentrations of the trapping agent P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 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<sub>6</sub>H<sub>5</sub>)<sub>3</sub> 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)<sub>2</sub>] and  $\Delta H_f^\circ$ (SSH<sub>2</sub>) 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)<sub>2</sub>S=S might be stable relative to their disulfide isomers while somewhere in the sequence Br<sub>2</sub>S<sub>2</sub>, Cl<sub>2</sub>S<sub>2</sub> one might find the two isomeric forms close together in  $\Delta H_f^\circ$  and hence coexisting. Both forms (RO)<sub>2</sub>S=S and ROSSOR are known.<sup>66</sup>

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<sup>64</sup> that optically active aryl-SO-CH<sub>2</sub>-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<sup>15.5</sup> s<sup>-1</sup>, 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<sub>6</sub>H<sub>5</sub>SO·) 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  $D_1$ <sup>a</sup>

Species	$D_1 + D_2$	Est $D_1$	Species	Sum of bond dissociation energies	Est $D_1$
F <sub>2</sub> SO	169	(87)	H <sub>2</sub> SO	121 ± 4	(63)
Cl <sub>2</sub> SO	110	(58)	Me <sub>2</sub> SO	105	(55 ± 2)
Br <sub>2</sub> SO	75	(40)	Et <sub>2</sub> SO	102	(54)
[F <sub>2</sub> SF <sub>2</sub> ]	105 ± 6	(83 ± 5)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO	133	66 ± 2
(HO) <sub>2</sub> SO	146 ± 3	(76)			
(MeO) <sub>2</sub> SO	125	(65)	F <sub>2</sub> SS	[> 129 ± 6]	
(EtO) <sub>2</sub> SO	125	(65)	Me <sub>2</sub> SS	95 ± 3	(47 ± 3)
(Et <sub>2</sub> N) <sub>2</sub> SO	122	(63)	H <sub>2</sub> SS	125 ± 7	(64 ± 7)
C <sub>6</sub> H <sub>5</sub> S-SOC <sub>6</sub> H <sub>5</sub>		36 <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> SO		67 ± 2

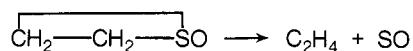
<sup>a</sup> Values in parentheses indicate estimated value of  $D_1$  based on  $D_1 - D_2 = 5 \pm 2$ ; see text. <sup>b</sup> This value differs from that reported of 34.5 kcal. The value of 36 kcal is derived from a revision of the experimental  $A$  factor. See text.

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

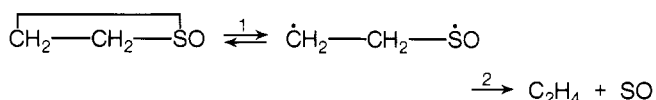
The general tendency in the sulfur bond strengths that we have considered so far is for the first of a pair of identical ligands to be more strongly bound than the second. The one datum that exists in the tetravalent sulfur group is for successive S-F bonds in SF<sub>4</sub>. From the data in Table VII we may estimate the first bond dissociation energy as  $83 \pm 5$  while the second becomes  $67 \pm 5$ , the difference being 16 kcal in favor of the first. On the other hand, for the thiosulfoxides of CH<sub>3</sub> 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<sub>2</sub>SO which is a radical chain process<sup>35</sup> can be employed to yield a value of  $DH^\circ(\text{CH}_3\text{-SO}(\text{CH}_3)) \geq 53$  kcal but  $\leq 56$  kcal. If we take the mean as  $55 \pm 2$  kcal then  $DH_2^\circ(\text{Me-SO}) = 50 \pm 2$  kcal which is in reasonable accord with the preceding observations on Me<sub>2</sub>SS and SF<sub>4</sub>. It would suggest  $D_1 - D_2 \sim 5 \pm 1$  kcal in Me<sub>2</sub>SO which in turn suggests that this might be applicable to the other sulfoxides as well.

Additional information comes from the pyrolysis of ethylene sulfoxide<sup>36</sup> which decomposes to ethylene + SO<sub>2</sub> + 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<sub>2</sub>SO,  $D_1 - D_2 = 5 \pm 1$ , then in Et<sub>2</sub>SO the C-S bond strength is 53 kcal. Thus the activation energy for ring opening to the biradical is only 34 kcal/mol

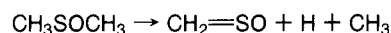


The second step in this process is exothermic by 11 kcal and probably has very little activation energy, thus making step 1 rate determining. If ring closing has only a few kilocalories of activation energy, the data would be compatible with the observations. A concerted process cannot be ruled out. 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<sup>37</sup> to give CH<sub>2</sub>=SO + C<sub>2</sub>H<sub>4</sub>. These are also in agreement with the biradical mechanism, reaction starting with C-S bond fission to give the unstable  $\cdot(\text{CH}_2)_3\dot{\text{S}}\text{O}$  biradical.

From these estimates of R-SOR' bond strengths we can also obtain an estimate of the  $\pi$  bond strength in CH<sub>2</sub>SO. Starting with

CH<sub>3</sub>SOCH<sub>3</sub> we can estimate the sum of the CH<sub>3</sub>-SOCH<sub>3</sub> ( $55 \pm 2$ ) and the C-H in the "unperturbed" methyl (98 kcal) as  $153 \pm 2$  kcal. But the overall reaction



is endothermic by  $110 \pm 5$  kcal. Hence the C-S  $\pi$  bond strength in CH<sub>2</sub>=SO is  $43 \pm 5$  kcal, appreciably less than the  $\pi$  bond strength of 56.5 we have calculated for CH<sub>2</sub>=S. This appears surprising since microwave studies<sup>37</sup> have shown identical C-S bond distances in CH<sub>2</sub>S and CH<sub>2</sub>SO. However the  $\pi$  bond estimates or  $\Delta H_f^\circ$  would have to be uncertain by over 10 kcal to bridge this gap. Even worse the required changes in  $\Delta H_f^\circ$  and  $E_\pi$  would have to be in unacceptable directions. Thus CH<sub>2</sub>S=O has an unusually high  $DH^\circ$  compared to other alkyl sulfoxides (Table VIII). If this were lowered by making the differences in  $\Delta H_f^\circ$  of CH<sub>2</sub>SO and CH<sub>2</sub>S smaller, the difference in  $\pi$  bond strengths would increase.

It is interesting to note that the C<sub>6</sub>H<sub>5</sub>SO radical has an estimated stabilization energy of only 3 kcal, considerably less than the 9.6 kcal observed in C<sub>6</sub>H<sub>5</sub>S and also less than the 13 found in C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>. This would be in accord with the weak  $\pi$  bond formation in CH<sub>2</sub>=SO just commented on.

#### IV. Hexavalent Sulfur

Hexavalent sulfur compounds can all be represented as derivatives of the >SF<sub>4</sub> or >SO<sub>2</sub> 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  $\pm 2$  kcal.<sup>8</sup> 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 → RFX) results in an increase in  $\Delta H_f^\circ$  of about 7 kcal. For X = H or CH<sub>3</sub> this reverses to -7 kcal. When X is more positive as in vinyl, phenyl, or carbonyl compounds, substitution of F for OH makes  $\Delta H_f^\circ$  more negative by about -2 kcal. SO<sub>2</sub> can be fitted into this sequence by observing that SO<sub>2</sub>(OH)<sub>2</sub> is 4 kcal less stable than SO<sub>2</sub>F<sub>2</sub> while FSO<sub>2</sub>(OH) is almost precisely the arithmetic mean.

Thus the SO<sub>2</sub> group seems to follow bond additivity rules to about  $\pm 1$  kcal with respect to elements of similar electronegativities such as Cl, F, and OH. On this basis we have estimated  $\Delta H_f^\circ$  for Cl(SO<sub>2</sub>)OH(g) as  $-133 \pm 1$  kcal (Table X). This appears to be compatible with the known  $\Delta H_f^\circ$  for the liquid and  $\Delta H_{\text{vap}}^\circ$  extrapolated from F(SO<sub>2</sub>)OH (Table X).

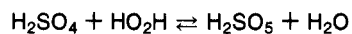
Data on the peroxy sulfuric acids exist only in aqueous solution. If we use the 40 kcal difference between  $\Delta H_f^\circ(\text{aq})$  and  $\Delta H_f^\circ(\text{g})$  for H<sub>2</sub>SO<sub>4</sub> as a starting point for extrapolation and

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

Ref	Species	$\Delta H_f^\circ_{298}$	$S^\circ_{298}$
(6)	SO <sub>3</sub>	-94.6	61.3
(6)	SO <sub>2</sub> F <sub>2</sub>	-181 ± 2	67.8
(6)	SO <sub>2</sub> Cl <sub>2</sub>	-84.8 ± 0.5	74.3
(6)	SO <sub>2</sub> ClF	[-133 ± 5]	72.3
(6)	SF <sub>6</sub>	-291.7	69.7
	SF <sub>4</sub> Cl	[-177]	
(6)	SF <sub>5</sub>	[-218 ± 3]	77 ± 2
(6)		-233 ± 5	
(7)	SF <sub>5</sub> Cl	-250.5	76.3
(4)	SO <sub>2</sub> H <sub>2</sub>	[-64 ± 4]	
(7, 6)	SO <sub>2</sub> (OH) <sub>2</sub> (l)	-194.5	37.5
	(aq)	-217.3	4.8
	(g)	-177.0 ± 2	69.1
	SF <sub>5</sub> OH	[-290 ± 2]	
(6)	FSO <sub>2</sub> (OH) (l)	-190.5	
	(g)	-180	71.0
(7)	CISO <sub>2</sub> (OH) (l)	-143.7	
	(g)	[-133 ± 1]	
	F(SO <sub>2</sub> )O·	[-127 ± 1.5]	[68.5 ± 1]
	HO(SO <sub>2</sub> )O·	[-125 ± 2.0]	[72 ± 1]
	SF <sub>4</sub> Cl <sub>2</sub>	[-205 ± 3]	[78 ± 1.5]
	·SO <sub>2</sub> H	[-98 ± 3]	[67 ± 1]
(4)	SO <sub>2</sub> (Me) <sub>2</sub>	-88.7	74.2
	SO <sub>2</sub> (Me)	[-55]	
(4)	SO <sub>2</sub> (OMe) <sub>2</sub>	-164	
(4)	SO <sub>2</sub> Ph <sub>2</sub>	-28.3	
(4)	SO <sub>2</sub> (OEt) <sub>2</sub>	-180.7	
(4)	SO <sub>2</sub> (Et) <sub>2</sub>	-102.5	
(4)	PhSO <sub>2</sub> -SO <sub>2</sub> Ph	-115	
	SO <sub>2</sub> CH <sub>2</sub>	[-69 ± 3]	
	c-(SO <sub>2</sub> ) <sub>3</sub>	-314	
	HO(SO <sub>2</sub> )O <sub>2</sub> H (aq)	[-192 ± 2]	
	(g)	[-152 ± 2]	[81.5 ± 1]
(7)	[HO(SO <sub>2</sub> )O] <sub>2</sub> (aq)	-320	59.3
	(g)	[-272 ± 2]	[104 ± 2]
(7)	HO(SO <sub>2</sub> ) <sub>2</sub> OH (aq)	-286.4	
	(g)	[-246 ± 5]	
	[F(SO <sub>2</sub> )O] <sub>2</sub> (g)	[-276 ± 3]	[101 ± 2]
	[HO(SO <sub>2</sub> ) <sub>2</sub> O]	[-282 ± 3]	
	c-O <sub>2</sub> S-O-O	[-76 ± 3]	
	Biradical SO <sub>4</sub>	[-73 ± 5]	
	HOSO <sub>2</sub> O <sub>2</sub> ·	[-114 ± 4]	
	SO <sub>2</sub> (O <sub>2</sub> H) <sub>2</sub>	[-127 ± 3]	
(60, 61)	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub>	[-37 ± 1]	
(60)	C <sub>6</sub> H <sub>5</sub> (SO <sub>2</sub> )SOC <sub>6</sub> H <sub>5</sub>	[-52 ± 2]	
	C <sub>6</sub> H <sub>5</sub> (SO <sub>2</sub> )SC <sub>6</sub> H <sub>5</sub>	[-22 ± 4]	
	SF <sub>5</sub> O·	[-236 ± 4]	
65	SF <sub>4</sub> O	[-226 ± 4]	
	(SF <sub>5</sub> O) <sub>2</sub>	-509 ± 5	

consider that H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is a very strong acid like H<sub>2</sub>SO<sub>4</sub>, then we estimate an aqueous - gas difference of 47 ± 3 kcal for H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and assign to H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 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  $\Delta H_f^\circ(\text{HO}(\text{SO}_2)\text{OOH})_{\text{gas}}$ . Further assuming that H<sub>2</sub>SO<sub>5</sub> has a difference in  $\Delta H_f^\circ$  between gas and aqueous states similar to H<sub>2</sub>SO<sub>4</sub> leads to  $\Delta H_f^\circ(\text{H}_2\text{SO}_5)_{\text{aq}} = -193 \pm 3$  kcal.

Monger and Redlich<sup>38</sup> have measured the equilibrium



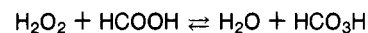
in aqueous solution and found an apparent equilibrium constant of about 0.1 at 25 °C which increased to about 0.2 at 75 °C. This latter would suggest  $\Delta H \approx +2.8$  kcal and require  $\Delta S \approx 5$  eu to account for  $\Delta G \approx 1.4$  kcal. This would lead to  $\Delta H_f^\circ(\text{H}_2\text{SO}_5)_{\text{aq}} = 188$  kcal in only fair agreement with our previous estimate. However, the best a priori estimates of  $\Delta S^\circ$  for this equilibrium yield a value of  $\approx +13$  eu and hence a  $\Delta H \approx -2.8$  eu. The in-

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

Species	Bond dissociation energy	Species	Bond dissociation energy
O <sub>2</sub> S=O	83.3	Me <sub>2</sub> SO=O	112
F <sub>2</sub> SO=O	110 ± 5	Et <sub>2</sub> SO=O	112
Cl <sub>2</sub> SO=O	95	Ph <sub>2</sub> SO=O	113
(HO) <sub>2</sub> SO=O	110 ± 3	PhSO=O	109
(MeO) <sub>2</sub> SO=O	108	(PhSO <sub>2</sub> )PhSO=O	122
(EtO) <sub>2</sub> SO=O	109	(PhSO)PhSO=O	122 ± 3
[F <sub>4</sub> S=F <sub>2</sub> ]	146 ± 5	(PhS)PhSO=O	115 ± 4
SF <sub>4</sub> =O	102 ± 6	CH <sub>2</sub> SO=O	[116 ± 6]

crease in  $K_{\text{aq}}$  with  $T$  would then have to be ascribed to an anomalously high value for  $\Delta C_p^\circ$ . This latter choice would give  $\Delta H_f^\circ(\text{H}_2\text{SO}_5)_{\text{aq}} = -193$  kcal, in excellent agreement with the earlier estimate. A reasonable reconciliation would be to use -191 ± 2 kcal which leads then to  $\Delta H_f^\circ_{298}(\text{H}_2\text{SO}_5)_{\text{gas}} = -151 \pm 3$  kcal and thence via group additivity to  $\Delta H_f^\circ_{298}(\text{H}_2\text{S}_2\text{O}_8)_{\text{gas}} = -270 \pm 6$  kcal. As a reasonable compromise among these values we shall use  $\Delta H_f^\circ_{298}(\text{H}_2\text{S}_2\text{O}_8)_{\text{gas}} = -272 \pm 2$  kcal. This then leads to  $\Delta H_f^\circ_{298}(\text{H}_2\text{SO}_5)_{\text{gas}} = -152 \pm 2$  and the other related values shown in Table X.

Let us note in passing that a similar equilibrium study of formic acid<sup>38</sup>



leads to a value for  $\Delta H_f^\circ(\text{HCO}_3\text{H})_{\text{gas}}$  in excellent agreement (± 1 kcal) with independent estimates from group additivity and kinetic data on diacyl peroxides.<sup>39</sup>

Now making use of our observation that F and OH form a homothermal pair relative to SO<sub>2</sub> with a  $\Delta(\Delta H_f^\circ)$  of 2 kcal we can estimate  $\Delta H_f^\circ[\text{F}(\text{SO}_2)\text{OO}(\text{SO}_2)\text{F}]_{\text{gas}} = -276 \pm 3$  kcal.

A number of studies have been made of the reversible dissociation of F<sub>2</sub>S<sub>2</sub>O<sub>6</sub> ⇌ 2FSO<sub>3</sub><sup>40</sup> and  $\Delta H$  and  $\Delta S$  are known with reasonable accuracy. From these measurements and the data already discussed we estimate  $\Delta H_f^\circ(\text{FSO}_3^\cdot)_{\text{gas}}$  and  $S^\circ(\text{FSO}_3^\cdot)$  shown in Table X as well as the other entropies shown. Finally using our F/OH rule we estimate  $\Delta H_f^\circ(\text{HOSO}_3^\cdot)_{\text{gas}} = -125 \pm 2.0$  kcal. Note that this yields a value for the O-H bond dissociation energy in H<sub>2</sub>SO<sub>4</sub> of 104 ± 3 kcal. This can be compared with  $\text{DH}^\circ(\text{RO-H})$  of 104 kcal in all the aliphatic alcohols and 106 kcal for  $\text{DH}^\circ(\text{RCO}_2\text{-H})$ . If we assume that the second O-H bond dissociation energy in H<sub>2</sub>SO<sub>4</sub> is not affected by removing the first, then we can calculate for the SO<sub>4</sub> biradical  $\Delta H_f^\circ(\text{SO}_4) = -73 \pm 4$ . This has some very interesting consequences which we shall pursue later in our discussion of the kinetics of SO<sub>2</sub> oxidation. For the moment let us simply note that SO<sub>4</sub> is a stable biradical with an O<sub>3</sub>S-O bond dissociation energy = 28 ± 4. At 25 °C we should expect SO<sub>4</sub> to be a long-lived species. It has a more stable cyclic analogue O<sub>2</sub>S-O-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<sub>4</sub> 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<sub>2</sub>O<sub>2</sub>, viz. 90 ± 1 kcal, then we can estimate that  $\Delta H_f^\circ_{298}[\text{HO}(\text{SO}_2)\text{OO}\cdot]_{\text{gas}} = -114 \pm 4$  kcal and that this radical is stable relative to dissociation into HOSO<sub>2</sub>· radical + O<sub>2</sub> 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<sub>2</sub>SO<sub>2</sub> and SO<sub>3</sub>. All of the other values

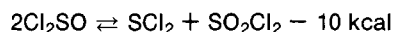
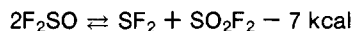
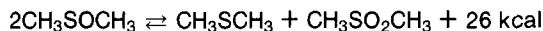
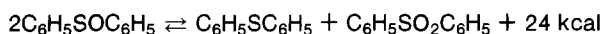


TABLE XII. X-SO<sub>2</sub> Single Bond Dissociation Energies in Sulfone Derivatives

Species	Bond dissociation energy	D <sub>1</sub> + D <sub>2</sub>	Species	Bond dissociation energy	D <sub>1</sub> + D <sub>2</sub>
CH <sub>3</sub> (SO <sub>2</sub> )-CH <sub>3</sub>	68	86	SO <sub>2</sub> F <sub>2</sub>	[100]	148
Et(SO <sub>2</sub> )-C <sub>2</sub> H <sub>5</sub>	68	84	SO <sub>2</sub> Cl <sub>2</sub>	[63]	75
CH <sub>3</sub> (SO <sub>2</sub> )-allyl	55	73	SO <sub>2</sub> (OH) <sub>2</sub>	[88]	125
CH <sub>3</sub> (SO <sub>2</sub> )-benzyl	56	74	SO <sub>2</sub> (F)(OH)		136
C <sub>6</sub> H <sub>5</sub> (SO <sub>2</sub> )C <sub>6</sub> H <sub>5</sub>	70	114	SO <sub>2</sub> (HO)(O <sub>2</sub> H)		95
CH <sub>3</sub> (SO <sub>2</sub> )-C <sub>6</sub> H <sub>5</sub>	83	101	[F(SF <sub>4</sub> )]-F	93 ± 3	147]
C <sub>6</sub> H <sub>5</sub> (SO <sub>2</sub> )-CH <sub>3</sub>	54	101		79 <sup>46</sup>	147 ± 3 <sup>46</sup>
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> -SO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	41 ± 1				
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> -SOC <sub>6</sub> H <sub>5</sub>	28 ± 1				

can be approximated as 111 ± 2 kcal. The exceptional stability of SF<sub>6</sub> is indicated by the high value of 146 ± 5 for removing two F atoms.

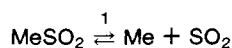
If we compare these R<sub>2</sub>SO=O bond dissociation energies with the values for R<sub>2</sub>S=O (Table VIII), we note that they are uniformly less by about 8 kcal for electronegative R. Even for the SO<sub>2</sub>Cl<sub>2</sub>/SOCl<sub>2</sub> pair this relation holds. This is not the case for the alkyl sulfones where the DH°(R<sub>2</sub>S=O) are uniformly less by about 23 kcal than DH°(R<sub>2</sub>SO=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



Kice<sup>60</sup> has noted the "bond-weakening effect" of SO on adjacent bonds ascribing the effect to the stability of the RSO 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 ΔH<sub>f</sub>° of the parent molecule and for the sulfones and sulfoxides illustrates again the principle of alternating polarity<sup>22,25</sup> which is so important in determining thermochemical stability. We have, in fact, noted that the C<sub>6</sub>H<sub>5</sub>SO radical has less stabilization energy than C<sub>6</sub>H<sub>5</sub>S· or C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>.

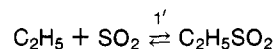
There are very few direct measurements of single bond dissociation energies for hexavalent sulfur compounds. Mackle and colleagues<sup>11</sup> used toluene carrier techniques to measure the rates of pyrolysis of alkyl and aryl sulfones. However, their assignments of Arrhenius parameters were inconsistent 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 ΔH<sub>f</sub>° data. From complex kinetic studies of the radiolysis of CH<sub>3</sub>SO<sub>2</sub>Cl in cyclohexane, Horowitz<sup>41</sup> has evaluated K<sub>eq</sub> for



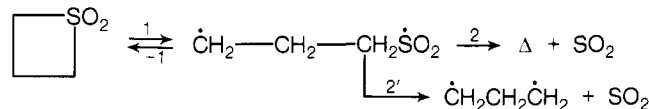
in the range 60–122 °C and from its temperature coefficient the values ΔH°<sub>1</sub> = 15.6 kcal/mol and ΔS°<sub>c</sub> = 23 eu. In the gas phase ΔS<sub>p</sub>° = 35 eu so that we could estimate that ΔH° = 17.2 kcal/mol would be the appropriate value for the gas phase dissociation in excellent agreement with the data in Table XII.

Further corroborating evidence for both these bond dissociation energies comes from the work of Good and Thynne<sup>47</sup> who measured the direct gas-phase equilibrium between CH<sub>3</sub> + SO<sub>2</sub>. They found ΔH<sub>1</sub> = 20 ± 2 while values for the equilibrium



gave ΔH<sub>1</sub>' = -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<sub>2</sub>. This would tend to support the analogy between CO (or CO<sub>2</sub>) and SO<sub>2</sub>. 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.

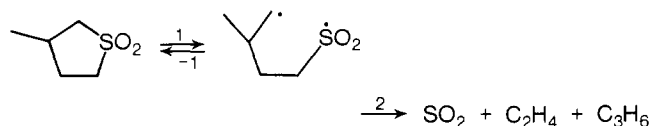
Cornell and Tsang<sup>42</sup> have conducted toluene carrier studies of the pyrolysis of trimethylene sulfone and 2-methylsulfolane. Very interestingly, for the former they find only cyclopropane and only traces of propylene, suggesting that trimethylene is not an intermediate. The high A factor of 10<sup>16.1</sup> s<sup>-1</sup> and E<sub>act</sub> = 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<sub>N</sub>2 displacement of SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>H<sub>4</sub> + CH<sub>2</sub>=SO<sub>2</sub>. From the lack of excess C<sub>2</sub>H<sub>4</sub> products we must conclude that the activation energy for this step exceeds 12 kcal. C<sub>2</sub>H<sub>4</sub> production from the sulfone could not be measured in the system because of the use of ethyl acetate → CH<sub>3</sub>COOH + C<sub>2</sub>H<sub>4</sub> 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 ΔH<sub>1</sub> ≈ 63 ± 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<sub>-1</sub> ~ 3 kcal with an expectedly low A factor of about 10<sup>12</sup> s<sup>-1</sup>. Since the energy to detach SO<sub>2</sub> 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	$\Delta H_f^\circ_{298}$	Group	$\Delta H_f^\circ_{298}$
S-(C <sub>d</sub> ) <sub>2</sub>	13.5	O-(H)(SO <sub>2</sub> )	-38.0 <sup>a</sup>
S-(C)(C <sub>d</sub> )	13.0	O-(H)(S)	-38.0 <sup>a</sup>
S-(H)(C <sub>d</sub> )	6.1	O-(H)(SO)	-38.0 <sup>a</sup>
S-(S) <sub>2</sub>	3.2	O-(SO <sub>2</sub> ) <sub>2</sub>	-4
S-(O) <sub>2</sub>	+9 ± 4	O-(O)(SO <sub>2</sub> )	3
		Ring corrections	
SO-(O) <sub>2</sub>	-51 ± 3	Thiophene	-16.3
SO <sub>2</sub> -(O) <sub>2</sub>	-101	Thiacyclopentene-2	2.0
SO <sub>2</sub> -(F)(O)	-142	c-S <sub>3</sub>	22.9
SO <sub>2</sub> -(Cl)(O)	-97	c-S <sub>4</sub>	18.4
		c-S <sub>6</sub>	5.3
		c-S <sub>8</sub>	-1.1

<sup>a</sup> 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<sub>5</sub> product which they could not identify which amounted to about 10% of the decomposition and could well be the cyclobutane derivative.

Recent<sup>67</sup> stereochemical studies on the pyrolysis of *cis*- and *trans*-1,2-dimethylsulfolanones 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  $50 \pm 2$  kcal which can be considered a reorganization energy of the SO<sub>2</sub> group. While there is no reason to expect this to be a constant independent of R in R<sub>2</sub>SO<sub>2</sub>, we can note that it is consistent with one of the few directly measured values of F-SO<sub>2</sub>F from shock tube studies.<sup>43</sup> 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<sub>2</sub>Cl<sub>2</sub> we estimate  $DH^\circ(\text{ClSO}_2\text{-Cl}) = 63$  shown in Table XII. In similar fashion reanalysis of the shock tube data on SF<sub>6</sub> leads to a F<sub>5</sub>S-F bond dissociation energy at room temperature of 93 kcal<sup>44</sup> which is also compatible with electron impact and electron affinity data on SF<sub>6</sub> and SF<sub>5</sub>.<sup>45</sup> This differs appreciably from the values selected by Hildenbrand<sup>46</sup> and the subject deserves further study. Note, however, that it yields  $D_1 - D_2 = 39$  for the SF<sub>4</sub> series.

Assignment of the constant difference for SO<sub>2</sub>R<sub>2</sub>,  $D_1 - D_2 = 50 \pm 2$  yields the bond strengths  $DH^\circ(\text{HOSO}_2\text{-OH}) = 88$  kcal shown in Table I and  $\Delta H_f^\circ(\text{SO}_2\text{OH}) = -98$  kcal.

The  $\Delta H_f^\circ$  deduced for the substituted SO<sub>3</sub> radicals permits us to draw some conclusions concerning SO<sub>3</sub>. From the data in Table X we can estimate  $DH^\circ(\text{F-SO}_2\text{O}\cdot) = 51 \pm 1.5$  kcal and  $DH^\circ(\text{HO-SO}_2\text{O}\cdot) = 39 \pm 2$  kcal. From  $\Delta H_f^\circ(\text{HO}\dot{\text{S}}\text{O}_2) = -98 \pm 3$  we can calculate an H-O bond dissociation energy of 81 kcal for the first bond in H<sub>2</sub>SO<sub>3</sub> and a value of a value of 55 kcal for  $DH^\circ[\text{H-O}\dot{\text{S}}\text{O}_2]$ . This gives 26 kcal as the reorganization energy of the isomeric SO<sub>3</sub> biradical  $\dot{\text{O}}\text{-SO-O}\cdot$  to SO<sub>3</sub>. This permits us

to calculate the R-O bond dissociation energies in the sulfites (RO)<sub>2</sub>SO. From the data in Table VII we find 89 kcal for  $D_1 + D_2$  for CH<sub>3</sub>-OSO<sub>2</sub>CH<sub>3</sub> and using  $D_1 - D_2 = 26$  kcal we estimate  $D_1 = 57.5$  kcal and  $D_2 = 31.5$  kcal.

$DH^\circ(\text{HO-SO}_2) = 36$  kcal which is only slightly weaker than the attachment of the OH bond to SO<sub>3</sub>.

In H<sub>2</sub>SO<sub>5</sub> 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<sub>2</sub>S<sub>2</sub>O<sub>8</sub> but typical of the differences in O-O bond strengths between peroxides and hydroperoxides. While  $\Delta H_f^\circ[\text{HO}(\text{SO})\text{O}_2\text{H}]_{\text{gas}}$  is not known, we can estimate upper and lower limits for it from  $\Delta H_f^\circ$  of the sulfone analogue HO(SO<sub>2</sub>)O<sub>2</sub>H 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  $111 \pm 2$  kcal. For the O substituent it is 15 kcal lower. With one OH and one OOH substituent we can guess that  $107 \pm 4$  might well bracket all likely values and thus give  $\Delta H_f^\circ(\text{HO}(\text{SO})\text{O}_2\text{H})_{\text{gas}} = 105 \pm 5$  kcal. This would make the O-O bond dissociation energy in this compound only  $16 \pm 6$  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<sub>2</sub>-O-SO<sub>2</sub>OH. For this bond we estimate  $DH^\circ(\text{HOSO}_2\text{-OSO}_2\text{H}) = 59 \pm 5$  kcal which explains why the various polymeric forms of SO<sub>3</sub> are quite stable in the absence of an acid or base catalyst.

The observation<sup>60,61</sup> that the C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>-SO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> bond fission has an activation energy of 41 kcal in inert solvents permits us to estimate  $H_f^\circ(\text{C}_6\text{H}_5\text{SO}_2\cdot)$  (Table XII) and a stabilization energy in this radical of  $14 \pm 1$  kcal, very similar to the stabilization energy in C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>· of 13 kcal. The stabilization observed in C<sub>6</sub>H<sub>5</sub>S· is some 4.5 kcal less than that in C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>, and this is probably to be expected since the source of the stability is the donation of charge from C<sub>6</sub>H<sub>5</sub> to the SO<sub>2</sub> 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<sub>2</sub> may be somewhat greater than C to S. If we assign a value of  $60 \pm 3$  kcal to this π bond, then we can estimate  $DH^\circ(\text{O}_2\dot{\text{S}}\text{CH}_2\text{-H}) = 38 \pm 3$  kcal and  $\Delta H_f^\circ(\text{CH}_2=\text{SO}_2) = -69 \pm 3$  kcal mol. This seems compatible with the S=O bond dissociation energies in similar compounds (Table XI).

For dithionic acid H<sub>2</sub>S<sub>2</sub>O<sub>6</sub> where  $\Delta H_f^\circ$  is known only approximately, we estimate  $DH^\circ(\text{HOSO}_2\text{-SO}_2\text{OH}) = 50 \pm 10$  kcal. One would anticipate from the analogy with (C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>)<sub>2</sub> that a more negative  $\Delta H_f^\circ$  and a stronger bond closer to 60 kcal would be more likely.

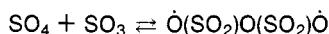
One of the more interesting compounds of sulfur is the SO<sub>4</sub> discussed earlier. The cyclic form is stable relative to the decomposition into SO<sub>2</sub> + O<sub>2</sub> by about  $5 \pm 3$  kcal but might have a high activation energy for such a decomposition because of spin forbiddenness. It is marginally more stable than the biradical SO<sub>4</sub> by about  $3 \pm 5$  kcal. The SO<sub>4</sub> biradical is stable relative to decomposition into SO<sub>3</sub> + O by 38 kcal and also stable relative to decomposition into SO<sub>2</sub> + O<sub>2</sub> by  $2 \pm 5$  kcal. If SO<sub>4</sub> 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<sub>4</sub> biradical is a stable species in the gas phase. Westenberg and deHaas<sup>49</sup> have shown that at room temperature O atoms and SO<sub>3</sub> 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<sub>3</sub>S-O bond would fulfill this requirement. The fate of SO<sub>4</sub> is somewhat mysterious in this system as it does not lead to SO<sub>2</sub> + O<sub>2</sub>. In fact, at much higher temperatures  $\text{O} + \text{SO}_3 \rightarrow \text{SO}_2 + \text{O}_2$  appears to be a slow reaction<sup>50,51</sup> with appreciable activation energy. One would expect from its manner of formation from

O + SO<sub>3</sub> that the stable form of biradical SO<sub>4</sub> would be the triplet state and this could account for its dynamic stability relative to cyclic peroxy-SO<sub>4</sub>.

One fate we might anticipate for radical SO<sub>4</sub> is self-polymerization to (SO<sub>4</sub>)<sub>n</sub> either linear or cyclic or polymerization with SO<sub>3</sub> to form linear or cyclic (SO<sub>3</sub>)<sub>n</sub>SO<sub>4</sub> with a peroxide linkage. The polymer (SO<sub>4</sub>)<sub>n</sub> could be looked upon as a copolymer of SO<sub>2</sub> and O<sub>2</sub>, and we can estimate its Δ*H*<sub>f</sub><sup>o</sup> from known groups as -95 kcal/mol SO<sub>4</sub>. Thus it would be stable by about 24 kcal/mol against decomposition into SO<sub>2</sub> + O<sub>2</sub> and it would be thermo-neutral with respect to the depolymerization into SO<sub>3</sub> + 1/2O<sub>2</sub>. The O-O bond in such a polymer is estimated to be 22 kcal/mol, like that in H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> so it could unzip at about room temperature.

The copolymer with SO<sub>3</sub> is expected to be more stable with an 11 kcal bond energy for the process



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.

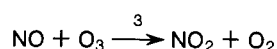
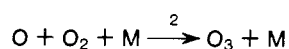
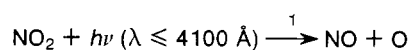
It has been reported<sup>52</sup> that when an electric discharge is passed through a SO<sub>2</sub>/O<sub>2</sub> mixture at 0.5 Torr (O<sub>2</sub> ≫ SO<sub>2</sub>) a white solid can be condensed with formula SO<sub>4</sub> and a melting point of +3 °C. On melting it evolves O<sub>2</sub> and leaves a liquid residue with the composition S<sub>2</sub>O<sub>7</sub>. 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.<sup>2,53</sup> 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.<sup>54</sup> An additional article of interest in examining low-temperature oxidation processes and their relation to aerosol formation has also appeared recently.<sup>55</sup> 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<sub>2</sub> also present in low concentrations (0.1–2.0 ppm). The process is accompanied by a catalytic production of O<sub>3</sub> (0.1 to 0.5 ppm maximum) and other oxidized species and usually aerosols.

Although photolysis produces O atoms from both NO<sub>2</sub> and O<sub>3</sub>, these are rapidly scavenged by O<sub>2</sub> molecules in a rapid process and rapidly achieve a very low photostationary concentration dominated by:

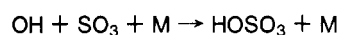
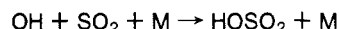


$$(\text{O})_{\text{ss}} = (I_0 \bar{\epsilon}_{\text{NO}_2}) / k_2(\text{O}_2)(\text{M})$$

*I*<sub>0</sub> is the flux of radiation and  $\bar{\epsilon}_{\text{NO}_2}$  the weighted extinction coefficient of NO<sub>2</sub>. Because of the low concentrations achieved, (~10<sup>5</sup>–10<sup>6</sup> atoms/cm<sup>3</sup> at noon) reactions of O atoms with ambient molecules will not be of interest unless their bimolecular rate constants exceed 10<sup>8</sup> L/mol·s. Instead it appears that other radicals such as OH, HO<sub>2</sub>, and RO<sub>2</sub> which react only very slowly or not at all with O<sub>2</sub> 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<sub>2</sub> and secondarily SO<sub>3</sub>. Both of these react with O atoms at rates whose apparent bimolecular rate constants of about 10<sup>8</sup> L/mol·s<sup>49,54</sup> are close to the minimum rate considered significant. In very bright sunlight at higher NO<sub>2</sub> concentrations these reactions might be important, but not otherwise.

The reaction of OH with both SO<sub>2</sub> and SO<sub>3</sub> is expected to be extremely rapid with rate constants approaching 10<sup>11</sup> and 10<sup>12</sup> L<sup>2</sup>/mol<sup>2</sup>·s:



The resulting radicals have DH<sup>o</sup>(HO-SO<sub>2</sub>) = 36 ± 3 kcal and DH<sup>o</sup>(HO-SO<sub>3</sub>) = 39 ± 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<sub>4</sub> 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<sub>2</sub>)ONO with DH<sup>o</sup>(HOSO<sub>2</sub>O-NO) = 22 ± 2 kcal and DH<sup>o</sup>(HOSO<sub>2</sub>-ONO) = 36 ± 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<sub>2</sub>O in the gas phase if the humidity is high enough.

HSO<sub>4</sub> will also react rapidly with NO<sub>2</sub> at almost every collision (*k* ~ 10<sup>10</sup> L/mol·s) to form nitryl sulfuric acid HO(SO<sub>2</sub>)ONO<sub>2</sub>. This species has an estimated Δ*H*<sub>f</sub><sup>o</sup><sub>298</sub> = -139 ± 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<sub>2</sub>O in the gas phase and hydrolyze readily on surfaces to H<sub>2</sub>SO<sub>4</sub> + HNO<sub>3</sub>.

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.

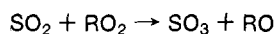
It has been suggested that HSO<sub>4</sub> can react with O<sub>2</sub> to form the peroxy radical HO(SO<sub>2</sub>)O<sub>3</sub>· which can then go on to react with NO to form NO<sub>2</sub> and HSO<sub>5</sub>.<sup>56</sup> Starting with our estimated Δ*H*<sub>f</sub><sup>o</sup>[HO(SO<sub>2</sub>)O<sub>3</sub>H] = -152 ± 2 we can estimate from group additivity rules for polyoxy compounds that Δ*H*<sub>f</sub><sup>o</sup>[HO(SO<sub>2</sub>)O<sub>3</sub>H] = -133 ± 3 kcal and Δ*H*<sub>f</sub><sup>o</sup>[HO(SO<sub>2</sub>)O<sub>4</sub>H] = -114 ± 3 kcal. In such polyoxides the RO<sub>*n*+2</sub>-H bond strength appears to be 90 ± 1 kcal as in H<sub>2</sub>O<sub>2</sub> so that we can estimate Δ*H*<sub>f</sub><sup>o</sup>[HO(SO<sub>2</sub>)O<sub>3</sub>·] = -95 ± 3 kcal. Thus the addition of O<sub>2</sub> to HSO<sub>4</sub> is endothermic by 20 ± 3.5 kcal and HSO<sub>6</sub>· is not expected to exist. In contrast the radical HOSO<sub>2</sub> can form a bond with O<sub>2</sub> with a dissociation energy of about 16 ± 5 kcal and hence the radical HSO<sub>5</sub> is expected to be a significant species in smoggy atmosphere containing SO<sub>2</sub>. DH<sup>o</sup>(HOSO<sub>3</sub>-O) is estimated to be 48 ± 5 kcal so that this radical should be capable of oxidizing NO to NO<sub>2</sub>. Note that the adduct with NO or NO<sub>2</sub> will not be stable. The reaction HSO<sub>5</sub> + NO<sub>2</sub> ⇌ NO<sub>3</sub> + HSO<sub>4</sub> is estimated to have Δ*H*<sup>o</sup> = 0 ± 4 kcal.

If we employ our rule that the reorganization energy of SO<sub>2</sub>

TABLE XIV.  $H_f^\circ$  for Some Acid Anhydrides and Their Heats of Hydrolysis in the Ideal Gas State

Ref	Anhydride	$\Delta H_f^\circ$	$\Delta H_{hyd}^\circ$
4	(CH <sub>3</sub> CO) <sub>2</sub> O	-137.1	-11.7
6	(NO <sub>2</sub> ) <sub>2</sub> O	2.7	-9.1
(Table X)	(HOSO <sub>2</sub> ) <sub>2</sub> O	-282 ± 3	-14 ± 3
7	Cl <sub>2</sub> O	21.0	-1 ± 5
(Table X)	HOSO <sub>2</sub> F	-180	-4
(Table X)	HOSO <sub>2</sub> Cl	-133	-8
(4)	CH <sub>3</sub> COF	-104	-6
(4)	CH <sub>3</sub> COCl	-58.9	-8.5
(4)	CH <sub>3</sub> COBr	-45.6	-8.6
(4)	CH <sub>3</sub> COI	-30.3	-8.9
(Table X)	SO <sub>2</sub> F <sub>2</sub>	-181 ± 2	-5.7 ± 2
(Table X)	SO <sub>2</sub> Cl <sub>2</sub>	-84.8	-12.4
Table I	HCOSH	-30	-7.5 ± 1
4	HCONH <sub>2</sub>	-44.5	1 ± 2
4	O <sub>2</sub> NOMe	-28.6	6.4
4	ONOMe	-15.6	7.1
15	CH <sub>3</sub> COOMe	-98.0	4.5
4	Me <sub>2</sub> O	-44.0	6.0
39	HO <sub>2</sub> OH	-13	7.0
Table X	HOSO <sub>2</sub> (OMe)	-170.5 ± 2	4.0

is 51 kcal then we can calculate  $\Delta H_f^\circ(\text{HO}_2\text{-SO}_2) = -73 \pm 4$  kcal. This suggests that the radicals HO<sub>2</sub> (and RO<sub>2</sub>) may react with SO<sub>2</sub> to form SO<sub>3</sub> + HO (and RO), respectively, with little or no activation energy. Thus SO<sub>2</sub> can, like NO, act as a catalyst for the conversion of relatively inert peroxy radicals into more active oxy radicals.



The intermediate adduct, RO<sub>2</sub>SO<sub>2</sub>, has a relatively weak RO-OSO<sub>2</sub> bond, 4 ± 4 kcal, and will not be stable.

The HSO<sub>3</sub> radical has a fairly strong HSO<sub>2</sub>-O bond which we estimate at about 97 ± 4 kcal; hence it will not oxidize NO<sub>2</sub>, NO, or SO<sub>2</sub>. We also calculate that it will not have any affinity for NO. However, it should react readily with NO<sub>2</sub> to form the fairly stable nitrosyl sulfuric acid:



As we have noted this will have a relatively short half-life at 300 K to dissociate into HSO<sub>4</sub> + 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<sub>2</sub> and SO<sub>3</sub>.  $\text{DH}^\circ(\text{SO}_3\text{-H}) = 55 \pm 3$  kcal so that one expects H atoms to add very rapidly to SO<sub>3</sub>. In high-temperature regimes the adduct is expected to have a very short lifetime for redissociation into SO<sub>2</sub> + OH for which  $\text{DH}^\circ = 36$  so that the reaction

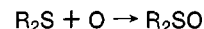


is expected to proceed very rapidly with little or no activation energy.

The reactions of H atoms with SO<sub>2</sub> 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<sub>2</sub>SO<sub>2</sub> has three isomeric forms (HO)<sub>2</sub>S, HSO(OH), and H<sub>2</sub>SO<sub>2</sub>. For these forms we have estimated  $\Delta H_f^\circ$  of -67 ± 5, -72 ± 5, and -64 ± 4, respectively. The radical HSO<sub>2</sub> has two isomeric forms H-SO<sub>2</sub> and HO-S=O for which by our various rules we can deduce  $\Delta H_f^\circ$  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<sub>2</sub> in flow systems have been made difficult by the very rapid wall recombination.<sup>57</sup> However, flame studies which have been re-

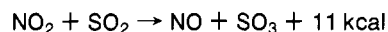
cently reviewed<sup>54</sup> indicate a fairly rapid three-body reversible recombination above 1600 K. This would be compatible with the 41-kcal bond energy.

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

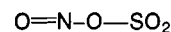


This reaction is very exothermic (Table VIII) and in the gas phase can be followed by dissociation of the weaker R-S bond. Gutman and coworkers<sup>58</sup> have shown that these reactions at room temperatures proceed with zero activation energy for RSH and R<sub>2</sub>S and have suggested that with H<sub>2</sub>S the excited adduct H<sub>2</sub>SO\* 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<sub>2</sub> and SO<sub>2</sub>:



Despite its exothermicity this reaction appears to have a surprisingly high activation energy of the order of 26 kcal.<sup>59</sup> Rate studies on this system have proven difficult because the bimolecular reaction of 2NO<sub>2</sub> → 2NO + O<sub>2</sub> 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:



We can estimate the  $\Delta H_f^\circ$  for this species by observing that  $\Delta H_f^\circ(\text{ONOSO}_3\text{H}) = -125 \pm 3$  kcal. If the S-OH bond dissociation energy in this anhydride is the same as its value in H<sub>2</sub>SO<sub>4</sub> (Table III), then we can calculate  $\Delta H_f^\circ(\text{ONO-SO}_2) = -46 \pm 4$  kcal. Thus the radical lies above SO<sub>2</sub> + NO<sub>2</sub> 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<sub>2</sub> with CO which is exothermic to form NO + CO<sub>2</sub> by 54 kcal but has an activation energy of 27 kcal. By similar methods we can estimate  $\Delta H_f^\circ(\text{O-NOCO}) = 1 \pm 3$  kcal so that the radical lies 19.5 ± 3 kcal above NO<sub>2</sub> + CO in  $\Delta H_f^\circ$  and the transfer reaction has an intrinsic activation energy of only 8 kcal.

## VI. Appendix: Methods of Estimation of $\Delta H_f^\circ$ of Acid Anhydrides

To estimate the  $\Delta H_f^\circ$  of the various sulfur and nitrogen oxy-acid 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 ( $\text{p}K_a$ ) of the two acids involved. Thus anhydrides of acids whose  $\text{p}K_a \leq 5$  seem to hydrolyze with  $\Delta H_{hyd} \approx -10 \pm 2$  kcal. As the  $\text{p}K_a$  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:



$$\Delta H_f^\circ [\text{HO}(\text{SO}_2)\text{ONO}_2] = -139 \pm 2$$

$$\Delta H_f^\circ [\text{CH}_3(\text{CO})\text{ONO}_2] = -65 \pm 2$$

On the same basis we would estimate:

$$\Delta H_f^\circ [\text{O}_2\text{N}-\text{NH}_2] = 15 \pm 2$$

$$\Delta H_f^\circ [\text{HO}(\text{SO}_2)\text{NH}_2] = -124 \pm 2$$

For HONO we can bracket the anhydride  $\Delta H_f^\circ$  between that of stable  $\text{N}_2\text{O}_3$  (+19.8 kcal) and separated  $\text{NO} + \text{NO}_2$  (+29.4 kcal). A reasonable choice would be  $\Delta H_f^\circ[(\text{ON})_2\text{O}] = 24 \pm 2$  kcal. Bond additivity would then yield  $\Delta H_f^\circ(\text{ONONO}_2) = 13.5 \pm 1$  kcal which can be compared to 2.5 kcal for the stable forms of  $\text{N}_2\text{O}_4$ .  $\Delta H_{\text{hyd}}^\circ[(\text{ON})_2\text{O}]$  is then -2.5 kcal while  $\Delta H_{\text{hyd}}^\circ[\text{O}-\text{NONO}_2] = -6$  kcal, both of which seem quite reasonable. On this basis, guided by the  $pK_a$  considerations, we would estimate:

$$\Delta H_f^\circ [\text{HO}(\text{SO}_2)\text{ONO}] = -129 \pm 2 \text{ kcal}$$

$$\Delta H_f^\circ [\text{CH}_3(\text{CO})\text{ONO}] = -56 \pm 2 \text{ kcal}$$

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## VII. References and Notes

- (1) Air Quality and Stationary Source Emission Control, National Research Council Report, Serial No. 94-4, U.S. Government Printing Office, Washington, D.C., 1975.
- (2) C. F. Cullis and M. F. R. Mulcahy, *Combust. Flame*, **18**, 225 (1975).
- (3) S. P. Sander and J. H. Seinfeld, *Environ. Sci. Technol.*, **10**, 1114 (1976).
- (4) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970.
- (5) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969.
- (6) "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Mich., 1966 plus later supplements to 1976.
- (7) "Selected Values of Chemical Thermodynamic Properties", Technical Note 270-3, U.S. Government Printing Office, Washington, D.C., 1968.
- (8) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
- (9) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).
- (10) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).
- (11) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS 21, U.S. Government Printing Office, Washington, D.C., 1970.
- (12) H. E. O'Neal and S. W. Benson, in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 17.
- (13) (a) F. Fehér and G. Winkhaus, *Z. Anorg. Chem.*, **292**, 210 (1957); (b) F. Fehér and G. Hitzemann, *ibid.*, **294**, 50 (1958).
- (14) A. Colussi and S. W. Benson, *Int. J. Chem. Kinet.*, **9**, 295 (1977).
- (15) S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, N.Y., 1976.
- (16) I. Kende, T. L. Pickering, and A. V. Tobolsky, *J. Am. Chem. Soc.*, **87**, 5582 (1965).
- (17) W. J. McKnight and A. V. Tobolsky, "Elemental Sulfur, Chemistry and Physics", Interscience Publishing Co., New York, N.Y., 1965, Chapter 1.
- (18) N. J. Friswell and B. G. Gowenlock in "Advances in Free Radical Chemistry", Vol. 2, Part II, G. H. Williams, Ed., Logos Press, London, 1967.
- (19) D. Detry, J. Drowart, P. Goldfinger, H. Keller, and H. Rickert, *Adv. Mass Spectrom.*, **4**, 499 (1968); *Z. Phys. Chem.*, **55**, 314 (1967).
- (20) R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Margott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", NSRDS-NBSID, U.S. Government Printing Office, Washington, D.C., 1967.
- (21) "Tables of Interatomic Distances and Configurations in Molecules and Ions", *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).
- (22) S. W. Benson and M. Luria, *J. Am. Chem. Soc.*, **97**, 704 (1975).
- (23) S. W. Benson and M. Luria, *J. Am. Chem. Soc.*, **97**, 3337 (1975).
- (24) S. W. Benson and M. Luria, *J. Am. Chem. Soc.*, **97**, 3342 (1975).
- (25) S. W. Benson, unpublished work.
- (26) A. Jones and F. P. Lossing, *J. Phys. Chem.*, **71**, 4111 (1967).
- (27) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).
- (28) H. Okabe, *J. Chem. Phys.*, **56**, 4381 (1972).
- (29) A. Colussi, F. Zabel, and S. W. Benson, *Int. J. Chem. Kinet.*, **9**, 161 (1977).
- (30) J. M. Pickard and A. S. Rodgers, *J. Am. Chem. Soc.*, **98**, 6115 (1976).
- (31) D. R. Johnson, F. Y. Powell, and W. H. Kirchoff, *J. Mol. Spectrosc.*, **39**, 136 (1970). They report on various kinetic sources of  $\text{CH}_2=\text{S}$  for use in microwave studies.
- (32) O. P. Strausz, H. E. Gunning, and J. W. Lown, "Chemical Kinetics", Vol. 5, Elsevier, Amsterdam, 1972, Chapter 6.
- (33) R. D. Brown, G. P. Pez, and M. F. O'Dwyer, *Aust. J. Chem.*, **18**, 627 (1965).
- (34) G. Höfle and J. E. Baldwin, *J. Am. Chem. Soc.*, **93**, 6307 (1971).
- (35) F. C. Thyrlion and G. Debecker, *Int. J. Chem. Kinet.*, **5**, 583 (1973).
- (36) G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.*, **88**, 2616 (1966).
- (37) E. Block, R. E. Penn, R. J. Olsen, and P. F. Sherwin, *J. Am. Chem. Soc.*, **98**, 1264 (1976).
- (38) J. M. Monger and O. Redlich, *J. Phys. Chem.*, **60**, 797 (1956).
- (39) S. W. Benson and R. Shaw, *Adv. Chem. Ser.*, No. 75, 288 (1968).
- (40) P. M. Nutkowitz and G. Vincow, *J. Am. Chem. Soc.*, **91**, 5956 (1969); earlier studies are referenced here.
- (41) A. Horowitz, *Int. J. Chem. Kinet.*, **8**, 709 (1976).
- (42) D. Cornell and W. Tsang, *Int. J. Chem. Kinet.*, **7**, 799 (1975).
- (43) K. L. Wray and E. V. Feldman, *J. Chem. Phys.*, **54**, 3445 (1971).
- (44) J. F. Bott and T. A. Jacobs, *J. Chem. Phys.*, **50**, 3850 (1969); J. Bott, *ibid.*, **54**, 181 (1971).
- (45) P. Harland and J. C. J. Thynne, *J. Phys. Chem.*, **73**, 4031 (1969); **75**, 3517 (1971).
- (46) D. L. Hildenbrand, *J. Phys. Chem.*, **77**, 897 (1973).
- (47) A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, **63**, 2708, 2720 (1967); the latter treats  $\text{C}_2\text{H}_5$  radicals.
- (48) P. A. G. O'Hare, *J. Chem. Phys.*, **52**, 2992 (1970).
- (49) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **62**, 725 (1975).
- (50) A. Jacob and C. A. Winkler, *J. Chem. Soc., Faraday Trans. 1*, **68**, 2077 (1972).
- (51) See discussion in ref 54, p 573.
- (52) J. P. Durant and B. Durant, "Introduction to Advanced Inorganic Chemistry", Wiley, New York, N.Y., 1962, p 821.
- (53) S. P. Sander and J. H. Seinfeld, *Environ. Sci. Technol.*, **10**, 1114 (1976), review the oxidation of  $\text{SO}_2$  in photochemical smog.
- (54) D. L. Baulch, D. D. Drysdale, J. Dixburg, and S. J. Grant, "Evaluated Kinetic Data for High Temperature Reactions", Vol. 3, Butterworths, London, 1976.
- (55) P. T. Roberts and S. K. Friedlander, *Environ. Sci. Technol.*, **10**, 573 (1976).
- (56) D. D. Davis, G. Smith, and G. Klauber, *Science*, **186**, 733 (1974); D. D. Davis, and G. Klauber, *Int. J. Chem. Kinet., Symp.*, **1**, 543 (1975).
- (57) R. W. Fair and B. A. Thrush, *Trans. Faraday Soc.*, **65**, 1550 (1969).
- (58) I. R. Slagle, R. E. Graham, and D. Gutman, *Int. J. Chem. Kinet.*, **8**, 451 (1976).
- (59) J. W. Armitage and C. F. Cullis, *Combust. Flame*, **16**, 125 (1971).
- (60) J. L. Kice, in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 24.
- (61) J. L. Kice and N. A. Favrostritsky, *J. Org. Chem.*, **35**, 114 (1970).
- (62) H. van Zwet and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **86**, 1143 (1967). The value shown is my own estimate from author's absolute rate constant.
- (63) H. van Zwet and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **87**, 45 (1968).
- (64) E. G. Miller and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4861 (1968). I have assigned an A factor of  $10^{15.5}$  to his rate constant and estimated  $E = 36$  kcal.
- (65) J. Czarnowski and H. J. Schumacher, *Int. J. Chem. Kinet.*, **9**, (1977).
- (66) Q. E. Thompson, et al., *J. Org. Chem.*, **30**, 2692, 2696 (1965).
- (67) W. L. Mock, I. Mehrotra, and J. A. Anderko, *J. Org. Chem.*, **40**, 1842 (1975).