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THE THERMOCHEMISTRY OF SULPHUR-CONTAINING MOLECULES AND RADICALS—II

THE DISSOCIATION ENERGIES OF BONDS INVOLVING SULPHUR: THE HEATS OF FORMATION OF SULPHUR-CONTAINING RADICALS

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Abstract—The values derived from pyrolysis rate and electron impact studies for the dissociation energies of carbon-sulphur bonds in organic thiols, sulphides and sulphones are critically discussed. Once these have been settled, they may be used, in conjunction with the heat of formation data given in Part I and other relevant thermochemical data, to derive values for the gas-phase heats of formation of certain sulphur-containing free radicals of key importance. These in turn, may be used to derive several whole new series of carbon-sulphur bond dissociation energies in molecules and radicals. Inspection of such series casts doubts upon the currently accepted values for the heats of formation of the n-butyl and t-butyl radicals and alternative values are suggested. The carbon-sulphur bond dissociation energies are much greater in RS radicals than in RSO_2 radicals. Values for the *mean* carbon-sulphur bond dissociation energies in sulphoxides are reported. The C=S bond dissociation energies in carbon disulphide and carbon oxysulphide are discussed. New series of sulphur-sulphur, hydrogen-sulphur and sulphur-oxygen bond dissociation energies are derived and tabulated. It is shown that, *ceteris paribus*, the dissociation energy of the sulphur-oxygen bond in sulphoxides is about 22 kcal $mole^{-1}$ lower than the dissociation energy of the first sulphur-oxygen bond in the corresponding sulphone. The variation of the sulphur-oxygen bond dissociation energy in sulphones, R_2SO_2, with variation in the nature of the R groups is demonstrated and discussed. This variation has not yet been given a satisfactory interpretation.

RELIABLE information about the energy changes associated with the formation or rupture of sulphur-containing bonds is of paramount importance to the development of our understanding and control of a considerable number of chemical processes of theoretical and commercial interest. Noteworthy among these are the vulcanization of rubber,[1] and protein transformations,[2] like the permanent setting of hair, the felting and shrinking of wool, the gelation of egg white and serum albumin, and the radiative deactivation of certain enzymes. All of these involve the cleavage or formation, or both, of H—S, C—S or S—S bonds. The physiological activities of the lactogenic and diuretic hormones are thought to have their origins in similar processes.[2] In the plastics industry sulphur compounds are being used increasingly in the manufacture of new polymers. Notable are the polysulphones,[3] formed by the co-polymerization of olefines with sulphur dioxide. Elucidation of the kinetic mechanism of this complex polymerization process requires reliable information about the thermodynamics of addition of sulphur dioxide to alkyl radicals and of the addition of olefines to alkane

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[1] See J. S. Ball, *Encyclopaedia of Chemical Technology*, Vol. 13. Interscience, N. York (1954).

[2] See A. J. Parker and N. Kharasch, *Chem. Rev.* **59**, 583 (1959).

[3] See F. S. Dainton and K. J. Ivin, *Quart. Rev.* **12**, 61 (1958).

sulphonyl radicals.[3,4] Such information has, as its starting point, a knowledge of the dissociation energies of the first and second C—S bonds in sulphones. The interpretation of certain peculiar features of the sulphochlorination of hydrocarbons rests upon similar thermochemical information.[4] In view of these considerations it is rather surprising that, until quite recently, comparatively little reliable information has been available on the energy properties of sulphur-containing bonds.

The dissociation energy, D(R—X), of a bond R—X is the energy change associated with the dissociation process:

$$RX \rightarrow R + X \qquad (1)$$

when all the constituents are in the ideal gas state. This energy change does, of course, depend upon the reaction temperature. In practice it is convenient to refer all such processes to a temperature of 298·15°K, the thermodynamic standard state temperature. Bond dissociation energies may be measured *directly* by several methods. For polyatomic molecules, such as concern us here, the most generally applicable are (1) the electron impact method; (2) the pyrolysis rate method. More direct dissociation energy values for bonds in polyatomic molecules have originated from the electron impact method than from any other. Although there are certain difficulties and ambiguities peculiar to it, these may be minimised by careful experimentation and interpretation and it is now generally reliable. Detailed reviews have been given by Hagstrum,[5] Craggs and McDowell,[6] and Field and Franklin,[7] among others. The pyrolysis rate method rests on the assumption that for reaction (1) the activation energy of the reverse or recombination reaction is zero. Thus the *activation energy* of the forward reaction is equated to the energy of the reaction. In other words, the dissociation energy, D(R—X), is identified with the activation energy term, E, in the Arrhenius equation. Experimental measurement of k, the first order rate constant for the dissociation process, thus forms the basis of the pyrolysis rate method. This field has been well reviewed in recent years by Steacie[8] and Szwarc.[9]

Primary C—S *bond dissociation energies*

The only reported direct measurements of the dissociation energies of carbon-sulphur bonds are those of Franklin and Lumpkin,[10] Braye *et al.*,[11–13] Busfield and Ivin,[14] and Palmer and Lossing.[15] Such studies are of key importance because, in conjunction with other relevent thermochemical data, they yield values for the gas-phase heats of formation of sulphur-containing free radicals. It follows from equation (1) that the dissociation energies of the first C—S bond in mercaptans, sulphides, sulphoxides and

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[4] W. K. Busfield, K. J. Ivin, H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.* **57**, 1064 (1961).
[5] H. D. Hagstrum, *Rev. Mod. Physics* **23**, 185 (1953).
[6] J. Craggs and C. A. McDowell, *Rep. Prog. Physics* **18**, 374 (1955).
[7] F. H. Field and J. L. Franklin, *Electron Impact Phenomena.* Academic Press (1957).
[8] E. R. Steacie, *Atomic and Free Radical Reactions* (2nd. Edition) Rheinhold, N. York (1954).
[9] M. Szwarc. *Chem. Rev.* **47**, 75 (1950).
[10] J. L. Franklin and H. E. Lumpkin, *J. Amer. Chem. Soc.* **74**, 1023 (1952).
[11] A. H. Sehon and B de B. Darwent, *J. Amer. Chem. Soc.* **76**, 4806 (1954).
[12] E. H. Braye, A. H. Sehon and B. de B. Darwent, *J. Amer Chem. Soc.* **77**, 5282 (1955).
[13] M. H. Back and A. H. Sehon, *Canad. J. Chem.* **38**, 1076 (1960).
[14] W. K. Busfield and K. J. Ivin, *Trans. Faraday Soc.* **57**, 1044 (1961).
[15] T. F. Palmer and F. P. Lossing, *J. Amer. Chem. Soc.* In press.

sulphones may be expressed in terms of equation (2) where the symbols have their usual significance and X = SH, SR, SOR, or SO_2R.

$$D(R'—X) = \Delta H_f(R')_g + \Delta H_f(X)_g - \Delta H_f(R'X)_g \tag{2}$$

Thus the $\Delta H_f(X)_g$ terms may be evaluated, provided the remaining terms are known. Reliable gas-phase heat of formation values $\Delta H_f(R')$ for a large number of hydrocarbon and other radicals are now available[16,17] and over one hundred $\Delta H_f(RX)_g$ terms are listed in Part I (Table 1). Only the directly determined D(R′—X) values are in short supply. Those that exist enable us to evaluate the gas-phase heats of formation of the radicals SH, SCH_3, SC_2H_5, SC_6H_5 and SO_2CH_3.

The SH *radical.* Some years ago Sehon and Darwent[11] used the "toluol carrier" technique to determine the rate constants of the processes:

$$RSH \rightarrow R + SH \tag{3}$$

for R = Me, Et, Bz, and derived the corresponding D(R—SH) values as already outlined. Their value, D(Bz—SH) = 53 ± 2 kcal mole,$^{-1}$ is, however, the only one which can be considered reliable.[18] When combined according to equation (2) with a value of 40 ± 4 kcal mole^{-1} for $\Delta H_f(Bz)_g$,[17] and a value of 21·9 ± 0·6 kcal mole^{-1} (see Part I, Table 1) for $\Delta H_f(BzSH)_g$ it yields a value of 34·9 ± 4·5 kcal mole^{-1} for $\Delta H_f(SH)_g$. This may be compared with the value, 35·2 ± 4·5 kcal mole^{-1}, implicit in the work of Franklin and Lumpkin[10]. These authors studied the following processes by the electron impact method:

$$RSH + e \rightarrow R^+ + SH + 2e \tag{4}$$

for R = Et, nPr, t-Bu. Subject to the assumption that the kinetic energy of the fragments is negligible, it is easy to show that:

$$\Delta H_f(SH)_g = \Delta H_f(RSH)_g - \Delta H_f(R^+)_g + A(R^+)_g \tag{5}$$

where A is the appearance potential of the ion R^+. The reliability of the $\Delta H_f(SH)_g$ values obtained thus depends on the accuracy of the appearance potential measurements and on the precision with which the other terms of equation (5) are known. Franklin and Lumpkin reported A—values of 11·69 eV, 11·12 eV and 9·96 eV for R = Et, n-Pr, and t-Bu respectively, and Stevenson[19] considers these accurate to within 0·1 eV. However, in deriving their $\Delta H_f(SH)_g$ values, Franklin and Lumpkin used unacceptable values for the $\Delta H_f(RSH)_g$ and $\Delta H_f(R^+)_g$ terms. Their work has, therefore, to be reinterpreted in the light of more recent information. In doing this the processes where R = n-Pr and t-Bu are omitted as they cannot be interpreted with any precision. Stevenson[19] has shown that in the fragmentation of normal hydrocarbons by electron impact, it is the *secondary and not the normal propyl* ion that invariably appears. Although he has presented arguments against this occurring in the fragmentation of 1-propanethiol these are now untenable as they are based on thermochemical and other data which have subsequently proved inaccurate. The process in which R = t-Bu is of limited value because of the considerable uncertainty in our knowledge of the true

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[16] P. W. Gray and A. Williams, *Chem. Rev.* **59**, 320 (1959).

[17] H. A. Skinner, *Modern Aspects of Thermochemistry*, R.I.C. Monograph No. 3. (1958).

[18] H. Mackle and R. T. B. McClean, *Trans. Faraday Soc.* **58**, 895 (1962).

[19] D. P. Stevenson, *Trans. Faraday Soc.* **49**, 867 (1953).

ionization potential and heat of formation of the t-Bu radical. There thus remains the process where R = Et. Here the appropriate terms in equation (5) are:

$$\Delta H_f(C_2H_5SH)_g = -11{\cdot}0 \text{ kcal mole}^{-1} \text{ (See Part I Table 1)}$$
$$A(C_2H_5^+) = 11{\cdot}69 \pm 0{\cdot}1 \text{ eV or } 269{\cdot}7 \pm 2 \text{ kcal;}$$
$$\Delta H_f(C_2H_5^+)_g = 223{\cdot}5 \pm 3{\cdot}5 \text{ kcal mole}^{-1} \text{ (See ref 18)}$$

When these are combined in equation (5) we obtain $\Delta H_f(SH)_g = 35{\cdot}2 \pm 4{\cdot}5$ kcal mole^{-1}, the value quoted above. In a very recent study, Palmer and Lossing[15] have reported a value of 10·50 ± 0·1 eV for the vertical ionization potential of the SH radical, and one of 14·43 ± 0·1 eV for the appearance potential of the ^+SH fragment ion from H_2S. These, when combined suitably with the value $\Delta H_f(H_2S) = -4{\cdot}82$ kcal mole^{-1} (See Part I table 2), yield a value of 33·7 ± 3 kcal mole^{-1} for $\Delta H_f(SH)_g$. We thus have three independent values for $\Delta H_f(SH)_g$ and these agree within the limits of experimental error. Here we choose a mean value of 34·6 ± 4 kcal mole^{-1} for $\Delta H_f(SH)_g$.

The SCH_3 *radical.* Braye *et al.*[12] determined $D(Bz - SCH_3) = 51{\cdot}5 \pm 2$ kcal mole^{-1} from kinetic studies in a manner exactly analogous to their work on benzyl mercaptan. When combined according to equation (2) with the currently accepted values for $\Delta H_f(Bz)_g$ and $\Delta H_f(Bz\ SCH_3)_g$ (See Part I Table 1), the above result yields a value of 30·5 ± 5 kcal mole^{-1} for $\Delta H_f(SCH_3)$. This agrees well with the value, $\Delta H_f(SCH_3)_g = 31{\cdot}8$ kcal mole^{-1}, reported recently by Palmer and Lossing[15], but contrasts with the value $\Delta H_f(SCH_3)_g = 36$ kcal mole^{-1}, implicit in the work of Franklin and Lumpkin[10]. This high value has to be rejected. Palmer and Lossing have shown that the appearance potentials, A_1 and A_2, of the ions in the following processes are not identical, as stated by Franklin and Lumpkin:

$$CH_3SCH_3 + e \xrightarrow{A_1} CH_3 + \overset{+}{S}CH_3 + 2\ e. \qquad (6)$$

$$CH_3S_2CH_3 + e \xrightarrow{A_2} CH_3S + \overset{+}{S}CH_2 + 2\ e. \qquad (7)$$

Here we choose the first value quoted above, $\Delta H_f(SCH_3)_g = 30{\cdot}5 \pm 5$ kcal mole^{-1} as the value, 31·8 kcal mole^{-1}, of Lossing and Palmer[15] is an upper limit.

The SC_2H_5 *radical.* Franklin and Lumpkin[10] studied the processes:

$$C_2H_5SC_2H_5 + e \xrightarrow{A_3} C_2H_5 + \overset{+}{S}C_2H_5 + 2\ e \qquad (8)$$

$$C_2H_5S_2C_2H_5 + e \xrightarrow{A_4} C_2H_5S + \overset{+}{S}C_2H_5 + 2\ e \qquad (9)$$

A_3 and A_4 represent the appearance potentials of the ions and:

$$\Delta H_f(SCH_3)_g = \Delta H_f(C_2H_5S_2C_2H_5)_g - \Delta H_f(C_2H_5SC_2H_5)_g - \Delta H_f(C_2H_5)_g - A_3 + A_4 \qquad (10)$$

Here, once again, Franklin and Lumpkin found A_3 equal to A_4. Thus, when the appropriate values (ref. 17 and Part I Table 1) for the remaining terms on the right-hand side of equation (10) are inserted, a value of 28 ± 3 kcal mole^{-1} for $\Delta H_f(SC_2H_5)$ is obtained. We consider this value to be somewhat high. In view of Palmer and Lossing's findings for A_1 and A_2, it is likely that A_3 is *not* equal to A_4 but about 2·5 kcal greater. If this is so, then equation (10) yields a value of 25·5 ± 3 kcal mole^{-1} for $\Delta H_f(SC_2H_5)$. This is the value we choose here.

The SPh *radical.* Recently Back and Sehon[13] have reported a tentative value of 60 kcal mole for D(PhS $-$ CH_3). This, in conjunction with the value listed in Part I (Table 1) for the gas-phase heat of formation of phenyl methyl sulphide, leads to a value of 51 kcal mole^{-1} for $\Delta H_f(\mathrm{PhS})_g$.

The SO_2CH_3 *radical.* Busfield and Ivin,[14] from studies of the kinetics of decomposition of dimethyl, benzyl methyl and allyl methyl sulphones, have derived D(R $-$ SO_2CH_3) values for R = Me, Bz, and Allyl. In conjunction with the appropriate values (Part I, Table 1 and ref. 17) for the first and third terms on the right-hand side of equation (2), these lead to values of $-61{\cdot}8 \pm 2$, $-57{\cdot}8 \pm 4$, and $-58{\cdot}7 \pm 5$ kcal mole^{-1} for $\Delta H_f(SO_2CH_3)_g$. The first of these is probably the most reliable. Here we choose a weighted mean value of -60 kcal mole^{-1}.

Our *direct* knowledge of the thermochemistry of sulphur-containing free radicals is limited to the above. We know nothing, for instance, about the formation heats of SOR type radicals. This is because we do not yet know the first C—S bond dissociation energy in any sulphoxide. There is thus a great need for pyrolysis rate and electron impact studies on a series of sulphoxides. It is equally desirable that the existing studies in the sulphide and sulphone series be considerably extended.

It will be clear from equation (2) that, once values have been established for the gas-phase heats of formation of the sulphur-containing free radicals, these may be used to obtain new D-values, provided the remaining terms on the right-hand side of the equation are known. Thus we can obtain D(R′ $-$ SH) values for R′ = CH_3, C_2H_5, n-C_3H_7, iso C_3H_7, nC_4H_9, t-C_4H_9, CH_3CO, Bz and C_6H_5, because the heats of formation of these radicals,[16,17] and the corresponding R′SH molecules (Part I, Table 1) are known. Likewise we can obtain a whole series of D(R′—SCH_3), D(R′—SC_2H_5) and D(R′—SO_2CH_3) values. These smoothed out to the nearest half-kilocalorie are set out in Table 1. Where available, the directly determined values are shown in the brackets marked by an asterisk. Unless otherwise listed, the uncertainty in the values in the first two columns is, in each case, ±5 kcalories. This large uncertainty is due mainly to the uncertainty in our knowledge of the $\Delta H_f(\mathrm{SR})_g$ terms, which in turn arises because of the existing uncertainty about the true value for the heat of formation of the benzyl radical. There is a great need for a precise determination of this latter quantity which has been the subject of dispute for so long. It is important to realise, however, that the *variation* of D(C $-$ S) with R′ is not subject to this uncertainity. Only the *absolute* D—values are affected. The uncertainty in the values in the two final columns is ±3 kcal unless otherwise listed.

TABLE 1. PRIMARY C—S BOND DISSOCIATION ENERGIES (KCAL MOLE^{-1})

R′	D(R′ $-$ SH)	D(R′ $-$ SCH_3)	D(R′ $-$ SC_2H_5)	D(R′ $-$ SO_2CH_3)
Me	73	72	72	62(60·5 ± 2)*
Et	71	70	71	64
n-Pr	73	72	72	—
i-Pr	70	69	70	62
n-Bu	74(71)	74(71)	75(72)	68(65)
t-Bu	66(69)	64(67)	66(69)	57(60)
Ph	78	77	77	73
Allyl	—	—	—	43·5(45·5 ± 2·5)*
Bz	(53 ± 2)*	(51·5 ± 2)*	53	48(49·5 ± 2·5)*
CH_3CO	77	—	—	—

Inspection of Table 1 leads to the following comments:

(a) For the same R′ radical D(R′—SR) is essentially constant for R = H, CH_3, C_2H_5. In other words, at least where R is a saturated hydrocarbon radical, $D(R^1$—SR) appears to be independent of R. We shall return to this point later.

(b) the C—S bond dissociation energy in sulphones, is, *ceteris paribus*, about 6 kcal $mole^{-1}$ smaller than that in mercaptans and sulphides. Although the relation between bond dissociation energy and bond energy term is not always simple, this would appear to support an earlier theoretical conclusion of Moffitt[20] regarding the corresponding bond energy terms.

(c) Proceeding down the columns, the trend is as expected with the exception of the cases where R′ = nBu or t-Bu. There is no apparent reason why D(nBu—S) should be greater than D(Et—S) or D(nPr—S). Indeed, we might even expect the contrary because of the probable greater reorganization energy of the nBu radical. It is possible that the anomaly arises because the currently accepted[17] value of 18·5 kcal $mole^{-1}$ for $\Delta H_f(nBu)_g$ is ~3–4 kcal $mole^{-1}$ too high. There is independent empirical evidence to support this contention, and we, therefore, choose a tentative value of 15 kcal $mole^{-1}$ for $\Delta H_f(nBu)_g$. This leads to the D(nBu—S) values shown in brackets in Table 1. The D(tBu—S) values are probably lower than the true ones. Even though there is some steric strain in the tBu group, it seems unlikely that the reorganization energy of the tBu radical is 5-6 kcal greater than that of the nBu radical. The D(tBu—S) values depend upon a value of 5 ± 3 kcal $mole^{-1}$ for $\Delta H_f(tBu)_g$. There is some evidence[21] that this value may be rather low, and that the true value is about 8 kcal $mole^{-1}$. If we accept this, we arrive at the D(tBu—S) values shown in brackets in Table 1. The Bz—S and Allyl—S bonds have the low dissociation energy values generally found for bonds involving the benzyl and allyl groups. The low values arise mainly because, immediately they are formed, the radicals become appreciably stabilized by delocalization of the odd electron throughout the conjugated system. The low value reported by Back and Sehon[13] for $D(CH_3$—SPh) indicates that the SPh radical also has an appreciable reorganization energy. Possibly the high D(Ph—S) and $D(CH_3CO$—S) values may be explained by applying ideas first used by Dewar and Schmeising[22] with regard to bond energy terms. These authors have argued that a change of hybridization from sp^3 to sp^2 on one of the carbon atoms of a carbon-carbon single bond increases the bond energy term by about 5 kcal $mole^{-1}$.

Secondary C—S *bond dissociation energies*

The dissociation energies of the C—S bonds in RS and RSO_2 type radicals may be evaluated via the following thermochemical equations, provided we know all the terms on the right-hand side:

$$D(R\text{—}S) = \Delta H_f(R)_g + \Delta H_f(S)_g - \Delta H_f(RS)_g \qquad (11)$$

$$D(R\text{—}SO_2) = \Delta H_f(R)_g + \Delta H_f(SO_2)_g - \Delta H_f(RSO_2)_g \qquad (12)$$

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[20] W. E. Moffitt, *Proc. Roy. Soc.* **A200**, 409 (1950).

[21] F. G. Szabo and T. Berces, *Acta Chem. Acad. Sci. Hungaricae* **22**, 461 (1960).

[22] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **11**, 96 (1960); **5**, 166 (1959); *Conference on Hyperconjugation*, p. 83. Bloomington (1958); Pergamon Press (1959).

TABLE 2. HEATS OF FORMATION OF SULPHUR-CONTAINING FREE RADICALS AT 25° (KCAL MOLE^{-1})

Radical	$\Delta H_f°$	Radical	$\Delta H_f°$
SH	34·6 ± 4	Me SO_2	−60 ± 3
SMe	30·5 ± 5	Et SO_2	(−69·2 ± 3)
SEt	25·5 ± 3	i-Pr SO_2	(−74·7 ± 3)
SPh	60	n-Bu SO_2	(−80·5 ± 3)
n-Pr S	(20 ± 3)	t-Bu SO_2	(−82·8 ± 3)
i-Pr S	(18 ± 3)	Allyl SO_2	(−44·0 ± 3)
n-Bu S	(15 ± 3)	Bz SO_2	(−38·5 ± 3)
t-Bu S	(11 ± 3)	–	–

We know $\Delta H_f(R)_g$ for a large number of hydrocarbon and other radicals.[17] The current best values for $\Delta H_f(SO_2)_g$ and $\Delta H_f(S)_g$ have already been discussed in Part 1, and are listed there in Table 2. As we have seen, the only $\Delta H_f(RS)_g$ and $\Delta H_f(RSO_2)_g$ terms which we know *directly* are for the radicals CH_3S, C_2H_5S, and CH_3SO_2. We can, however, make plausible estimates of the heats of formation of certain other RS and RSO_2 radicals via the following argument We have already noted (Table 1) that D(R′—SR) appears to be independent of R, at least when R is a saturated hydrocarbon radical. Furthermore, for R′ = Me, Et, or n-Pr, it has a mean value of 72 ± 1 kcal mole^{-1}. Thus, for R′ = Me, Et, or n-Pr, we may write:

$$\Delta H_f(R')_g + \Delta H_f(SR)_g - \Delta H_f(R'\ SR)_g = 72 \text{ kcal} \tag{13}$$

Likewise, if we assume that D(R′ − SO_2R) is also independent of R within the limits stated above, we may write:

$$\Delta H_f(CH_3)_g + \Delta H_f(RSO_2)_g - \Delta H_f(CH_3SO_2R)_g = 62 \text{ kcal} \tag{14}$$

These equations enable us to evaluate the radical heats of formation shown in brackets in Table 2. The values without brackets are those which have been experimentally determined as already discussed. We may now proceed to evaluate the C—S bond dissociation energies in the radicals using equations (11) and (12). The results smoothed to the nearest half-kilocalorie are given in Table 3.

There is a surprisingly large difference between D(R—S) and D(R—SO_2). It might be argued that this arises because the ground state of the sulphur atom is a triplet whereas that of sulphur dioxide is a singlet, and that the following processes are

TABLE 3. C—S BOND DISSOCIATION ENERGIES IN RADICALS (KCAL MOLE^{-1})

R	D(R − S)	D(R − SO_2)
Me	68·0	21·5
Et	66·0	23·5
n-Pr	68·0	–
i-Pr	65·0	20·5
n-Bu	66·0	24·5[a]
t-Bu	63·0	20·0[b]
Allyl	–	3·0
Bz.	–	7·5

[a] Based on a value of 15 kcal mole^{-1} for ΔH_f (nBu).

[b] Based on a value of 8 kcal mole^{-1} for ΔH_f (tBu).

more strictly comparable:

$$RS \rightarrow R + S \qquad \Delta H_1 \tag{15}$$

$$RSO_2 \rightarrow R + :SO_2 \qquad \Delta H_2 \tag{16}$$

Here $:SO_2$ denotes the lowest triplet state of SO_2 which lies 73·4 kcal[23] above the grounds tate. ΔH_2 thus has a value of 95 kcal, while ΔH_1 remains about 66–67 kcal. Once again, therefore, the difference is large but now in the opposite direction.

Inspection of Tables 1 and 3 reveals another marked contrast in behaviour between sulphides and sulphones. There is a comparatively small difference of 4–5 kcal $mole^{-1}$ between the first and second C—S bond dissociation energies in sulphides, whereas in sulphones this difference is of the order of 40 kcal $mole.^{-1}$

Mean C—S *bond dissociation energies in sulphoxides*

Since we have no direct knowledge of heat of formation of any SOR-type radical we cannot begin to set up values for the first and second C—S bond dissociation energies in sulphoxides. We can, however, deduce a series of values for the *mean* of these two quantities.

Consider the following bond dissociation process:

$$R_1R_2SO\ (g) \xrightarrow{\Delta H} R_1(g) + R_2\ (g) + SO\ (g) \tag{17}$$

Here ΔH may be identified with the sum of the dissociation energies of the two C—S bonds. In other words $\frac{1}{2}\Delta H$ is the *mean* C—S bond dissociation energy, $\bar{D}$(C—S) and:

$$\Delta H = \Delta H_f(R_1)_g + \Delta H_f(R_2)_g + \Delta H_f(SO)_g - \Delta H_f(R_1R_2SO)_g \tag{18}$$

Choosing the heats of formation of the radicals as before, a value of 0·5 ± 0·5 kcal $mole^{-1}$ for the heat of formation of gaseous SO (See Part I, Table 2), and the appropriate values (Part I, Table 1), for the $\Delta H_f(R_1R_2SO)_g$ terms we arrive at the $\bar{D}$(C—S) values shown in Table 4.

TABLE 4. MEAN C—S BOND DISSOCIATION ENERGIES IN SULPHOXIDES (KCAL $MOLE^{-1}$)

R_1	R_2	$\bar{D}$(C—S)	R_1	R_2	D(C—S)
Me	Me	50·3	Et	t-Bu	49·7
Et	Et	50·2	Et	Allyl	40·8
n-Pr	n-Pr	50·1	Et	Ph	56·9

C=S *Bond dissociation energies*

Consider the gas-phase processes:

$$CS_2 \rightarrow CS + S\ \Delta H_1 = 93 \pm 15 \tag{19}$$

$$COS \rightarrow CO + S\ \Delta H_2 = 72{\cdot}6 \pm 1 \tag{20}$$

$$CO_2 \rightarrow CO + O\ \Delta H_3 = 127{\cdot}2 \pm 0{\cdot}6 \tag{21}$$

$$COS \rightarrow CS + O\ \Delta H_4 = 148 \pm 15 \tag{22}$$

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[23] R. K. Russell, *Phys. Rev.* **94** 805 (1954).

The ΔH-terms are readily computed from the relevant data of Tables 1 and 2 of Part I. Clearly ΔH_1 and ΔH_2 represent the C=S bond dissociation energies in carbon disulphide and carbon oxysulphide respectively. Thus, if the mean value chosen for the heat of formation of carbon monosulphide is correct, substitution of one of the sulphur atoms of carbon disulphide by an oxygen atom causes a very appreciable weakening (20 kcal mole^{-1}) of the remaining C=S bond. At the same time, as inspection of the ΔH_3 and ΔH_4 terms shows, the C=O bond in carbon oxysulphide would appear to be correspondingly stronger than its counterpart in carbon dioxide. The magnitude of these effects is difficult to understand. It is not paralleled by any significant variation of the corresponding C=S and C=O bond lengths[24] or force constants.[25] In fact it simply confirms our earlier doubts concerning the reliability of the value listed in Part I, Table 2 for the heat of formation of carbon monosulphide.

S—S *Bond dissociation energies*

For S—S bond dissociation energies, equation (2) takes the form:

$$\mathrm{D(R'S{-}SR)} = \Delta H_f(\mathrm{R'S})_g + \Delta H_f(\mathrm{SR})_g - \Delta H_f(\mathrm{R'SSR})_g \qquad (23)$$

Using the radical heats of formation of Table 2, and the gas-phase heats of formation of the relevant disulphides (Part 1, Tables 1 and 2), we thus derive: D(HS − SH) = 65, D(MeS—SMe) = 67, D(EtS—SEt) = 69, D(nPr S—SnPr) = 68. The units are kcal mole^{-1} and the uncertainty is ±6 kcal in each instance. These values may be contrasted with the values, 51, 37, 32 and 35 kcal mole^{-1} quoted[26] for the dissociation energies of the O—O bonds in the corresponding peroxides. The greater strength of the S—S bonds is no doubt due, partly at least to d_π-p_π overlap[27] between the adjacent sulphur atoms.

H—S *Bond dissociation energies*

For H—S bonds equation (2) takes the form:

$$\mathrm{D(H{-}SR)} = \Delta H_f(H)_g + \Delta H_f(\mathrm{SR})_g - \Delta H_f(\mathrm{HSR})_g \qquad (24)$$

Thus, once again, using the relevant data of Part I (Tables 1, 2) and Table 2 of the present paper, we may derive the D(H—SR) values shown in Table 5.

TABLE 5. H—S BOND DISSOCIATION ENERGIES (KCAL MOLE^{-1})

R	D(H—SR)	R	D(H—SR)
H	92 ± 5	nPr	88·0 ± 5
Me	88 ± 5	iPr	88·0 ± 5
Et	88·5 ± 5	nBu	88·0 ± 5

Apart from R = H, D(H—SR) appears to be independent of R, at least for saturated hydrocarbon radicals.

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[24] L. E. Sutton. *Tables of Interatomic Distances; Chem. Soc. Special Publication* No. **11** (1958).

[25] H. J. Callomon, D. C. McKean and H. W. Thompson, *Proc. Roy. Soc.* **A208** 341 (1951)

[26] T. L. Cottrell, *The Strengths of Chemical Bonds* (2nd. Edition, Butterworths, London (1958).

[27] H. KREBS, *Zeit. Naturforsch.* **12B** 795 (1957); O. Foss and O. Tjomsland. *Acta Chem. Scand.* **12**, 44 1805 (1958).

S—O *Bond dissociation energies in sulphoxides and sulphones*

Consider the bond dissociation process:

$$R_1R_2SO\,(g) \xrightarrow{\Delta H_1} R_1R_2S\,(g) + O\,(g) \tag{25}$$

Clearly ΔH_1 represents $D(R_1R_2S—O)$ and

$$D(R_1R_2S—O) = \Delta H_f(R_1R_2S)_g + \Delta H_f(O)_g - \Delta H_f(R_1R_2SO)_g \tag{26}$$

Inserting the appropriate values (Part 1, Tables 1 and 2), for the terms on the right-hand side of equation (26), we get the values listed in Table 6 for the S—O bond dissociation energy in sulphoxides. Evidently the nature of the groups, R_1 and R_2, at least when they are hydrocarbons, has little or no effect on the sulphur-oxygen bond dissociation energy. There is spectroscopic[28] and theoretical support[28,20] for this conclusion. The strength of the sulphur-oxygen bond appears to depend to some extent on its polarity, and this would not be expected to vary significantly in the sulphoxides listed above. The dissociation energy, 89–90 kcal mole^{-1}, of the sulphur-oxygen bond in sulphoxides may be contrasted with that of sulphur monoxide,[29] 123·5 kcal mole^{-1}, and that of the first sulphur-oxygen bond in sulphur dioxide, 131 kcal mole^{-1}. This latter value is readily computed using the data of Part I (Table 2).

TABLE 6. S—O BOND DISSOCIATION ENERGIES IN SULPHOXIDES (KCAL MOLE^{-1})

R_1	R_2	D(S—O)	R_1	R_2	D(S—O).
Me	Me	86 ± 2	Et	t-Bu	90 ± 1
Et	Et	89 ± 1	Et	Allyl	89 ± 1
n-Pr	n-Pr	90 ± 1	Ph	Ph	89 ± 1

Consider also the bond dissociation process:

$$R_1R_2SO_2\,(g) \xrightarrow{\Delta H_2} R_1R_2S\,(g) + 2O\,(g) \tag{27}$$

Clearly ΔH_2 may be identified with the *sum* of the dissociation energies of the two S—O bonds in sulphones, and may be expressed in the form:

$$\Delta H_2 = \Delta H_f(R_1R_2S)_g + 2\Delta H_f(O)_g - \Delta H_f(R_1R_2SO_2)_g \tag{28}$$

Inserting the appropriate values (Part 1, Tables 1 and 2), for the terms on the right-hand side of equation (28), we obtain the ΔH_2 values given in Table 7. Once again,

TABLE 7. ΔH_2 VALUES FOR SULPHONES (KCAL MOLE^{-1})

R_1	R_2	ΔH_2	R_1	R_2	ΔH_2
Me	Et	204 ± 2	Me	n-Bu	204 ± 2
Et	Et	204 ± 2	Me	t-Bu	202 ± 2
Me	i-Pr	202 ± 2	Et	t-Bu	202 ± 2
n-Pr	n-Pr	202 ± 2	Et	Allyl	202 ± 2
n-Bu	n-Bu	202 ± 2	Me	Ph	206 ± 2
i-Bu	i-Bu	202 ± 2	Me	Bz	206 ± 2
t-Bu	t-Bu	200 ± 2	Ph	Ph	204 ± 2
—	—	— —	Bz	Bz	202 ± 2

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[28] D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.* 2442 (1949).

[29] R. G. W. Norrish and G. A. Oldershaw, *Proc. Roy. Soc.* A249 498 (1958).

when R_1 and R_2 are hydrocarbons, ΔH_2 is essentially independent of their nature. Thus the sum of the dissociation energies of the two S—O bonds in sulphones has a mean value of 202 ± 2 kcal mole^{-1}.

There is one final consideration which appears to pose an interesting problem in bond theory. It is this. Since the heat, ΔH_1 or D(R_1R_2S—O), of the dissociation process represented by equation (25) may also be identified with the dissociation energy of the *second* sulphur-oxygen bond in the sulphones, the dissociation energy of the *first* sulphur-oxygen bond is simply the difference between ΔH_2 and ΔH_1. It has a mean value of 112·5 ± 2·5 kcal mole^{-1} for the sulphones listed above. The dissociation energy of the first sulphur oxygen bond in a sulphone is thus about 22 kcal greater than that of the sulphur-oxygen bond in the corresponding sulphoxide. The spectroscopic,[28] length,[24] dipole moment[30] and theoretical[20] data for the undissociated bonds correlate with this result.

When, however, we come to examine sulphones with significantly different R groups a new situation developes. Quite recently Claydon and Mortimer[31] have determined the first sulphur-oxygen bond dissociation energies in the sulphones, Cl_2SO_2 and $(Et_2N)_2SO_2$ to be 94·6 ± 0·5 and 130·8 ± 4·2 kcal mole^{-1} respectively. We thus have the situation set out in the Table below:

Compound	D(SO) kcal mole^{-1}	K(SO) × 10^5 dynes cm^{-1}	P(SO) (calc)
Cl_2SO_2	94·6 ± 1	9·93	1·0
$(Alkyl)_2SO_2$	112·5 ± 2·5	6·95	0·82
$(Et_2N)_2SO_2$	130·8 ± 4·2	—	—

Here D(SO) represents the first SO bond dissociation energy, k(SO) represents the bond force constant (see refs 20 and 28 and 32) and P(SO) represents the mobile bond order (see ref 20). It is clear from the Table that here there is no correlation between the bond dissociation energy values and quantities like force constant and mobile bond order which are properties of the undissociated bond. However, this lack of correlation need cause little surprise. The force constant is a measure of the resistance of a bond to *small* perturbations; whereas the bond dissociation energy is a measure of the *large* perturbations required for complete rupture of the bond. Thus, although larger force constants tend to be associated with larger dissociation energies, this is not always necessarily so.[26] Furthermore, in view of the drastic assumptions and approximations involved in the calculation of mobile bond orders and the considerable electronic reorganization associated with bond rupture, the existence of a definite correlation between bond order and bond dissociation energy would be more surprising than its absence.

What *is* difficult to explain, however, is the bond dissociation energy trend shown in the Table. A similar trend exists for the analogous phosphoryl compounds,[31] R_3PO. In the series R = Cl, Me, Et_2N, the respective D(P=O) values are 127·5 ± 0·5; 139·3 ± 3·0; and 156·0 ± 3 kcal mole^{-1}. It has been suggested that d_π-p_π-bonding[33]

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[30] G. M. Phillips, J. S. Hunter and L. E. Sutton, *J. Chem. Soc.* 146 (1945).

[31] A. P. Claydon and C. L. Mortimer, *J. Chem. Soc.* 3212 (1962).

[32] K. Venkateswarlu and P. T. Sambandam, *Zeit. Physik. Chem.* **13** 235 (1957).

[33] See D. P. Craig, A. MacColl, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.* 332 (1954).

or back co-ordination from the R groups to the phosphorous atom, is increased in $R_3P{=}O$ as compared with R_3P, causing a strengthening of the P—R bonds in the phosphoryl compounds which will, of course, be included in the dissociation energy, D(P=O). This effect is likely to be greater for R = Et_2N than for R = Cl because of the stronger donor tendency of the nitrogen atom. Thus we have what might appear to be a plausible *qualitative* explanation of why D(P = O) is greater when R = Et_2N than when R = Cl. An identical argument can be applied to D(S=O) in Cl_2SO_2 and $(Et_2N)_2SO_2$. However, the values for D(P=O) and D(S=O) in $(CH_3)_3PO$ and $(CH_3)_2SO_2$ appear to invalidate such an approach. Here there is no possibility of d_π-p_π-bonding. We would thus expect D(P=O) and D(S=O) in these compounds to have the *lowest* values of their respective series. In fact, as the figures quoted above show, they undoubtedly have *intermediate* values.