619. *Heats of Formation and Bond Energies. Part VIII.* Diethylaminotrimethylsilane,* NN′-*Dithiodiethylamine,* NN′-*Thionylbisdiethylamine, and* NN′-*Sulphurylbisdiethylamine.*

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Values are reported for the heats of reaction between liquid triethylamine and liquid chlorotrimethylsilane, sulphur monochloride, thionyl chloride, and sulphuryl chloride. These data are used to calculate the $\Delta H_f°$ values: $(Et_2N)_2S_2$ (liq.) = $-29{\cdot}4 \pm 1{\cdot}6$; $(Et_2N)_2SO$ (liq.) = $-75{\cdot}9 \pm 1{\cdot}7$; $(Et_2N)_2SO_2$ (liq.) = $-149{\cdot}4 \pm 2{\cdot}3$ kcal./mole; and the difference $\Delta H_f°(Me_3SiCl$, liq.) $-$ $\Delta H_f°(Me_3Si{\cdot}NEt_2$, liq.) = $+4{\cdot}1 \pm 1{\cdot}3$ kcal./mole. Comment is made on the differences in bond energies $[E(A\text{–}Cl) - E(A\text{–}N)]$, where A is silicon, phosphorus, or sulphur. The dissociation energies, $D(S{=}O)$, for the gas-phase process $R_2SO_2 \longrightarrow R_2SO + O$ are calculated for R = Cl, NEt_2, and Me, and the variation in these values is considered.

Craig, Maccoll, Nyholm, Orgel, and Sutton [1] have drawn attention to the use of *d*-orbitals in bonding and have suggested that π-bonding involving *d*-orbitals is likely to occur in compounds of silicon, phosphorus, and sulphur. Where these atoms are bonded to " first-row " elements, such as carbon, nitrogen, or to the halogens, this bonding is probably of the type d_π–p_π, involving an ultimate *d*-orbital of the " second-row " element and a *p*-orbital of the " first-row " element. In compounds of the type R_4Si, R_3P, and R_2S this d_π–p_π-bonding will be dative, a " back co-ordination " [2] from the donor atom of the R group to the silicon, phosphorus, or sulphur atom. The contribution of this d_π–p_π-bonding to the strength of the R–P and R–S bonds is likely to be increased in the phosphoryl, thionyl, and sulphuryl derivatives, R_3PO, R_2SO, and R_2SO_2, because of the attachment of the highly electronegative oxygen atom.

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* Part VII, *J.*, 1962, 2932.

[1] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

[2] Sidgwick, " The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, p. 606.

In Parts I,[3] II,[4] and III [5] of this series, the heats of formation of a number of organophosphorus compounds have been reported. In this paper the heats of formation of some organosilicon and organosulphur compounds are reported. These data have been used to calculate bond energies and bond-dissociation energies. It is suggested that variations in these quantities are due, in part, to differing amounts of d_π–p_π-bonding in the molecules.

The reactions between an excess of diethylamine, either liquid or in cyclohexane solution, and chlorotrimethylsilane,[6] sulphur monochloride, thionyl chloride, and sulphuryl chloride [7] are rapid and quantitative, at 25°, according to:

$$\mathrm{Me_3SiCl\ (liq.) + 2Et_2NH\ (cyclohexane\ soln.) \longrightarrow Me_3Si{\cdot}NEt_2\ (cyclohexane\ soln.) + Et_2NH_2Cl\ (cryst.)} \quad (1)$$

$$\mathrm{S_2Cl_2\ (liq.) + 4Et_2NH\ (cyclohexane\ soln.) \longrightarrow (Et_2N)_2S_2\ (cyclohexane\ soln.) + 2Et_2NH_2Cl\ (cryst.)} \quad (2)$$

$$\mathrm{SOCl_2\ (liq.) + 4Et_2NH\ (liq.) \longrightarrow (Et_2N)_2SO\ (diethylamine\ soln.) + 2Et_2NH_2Cl\ (cryst.)} \quad (3)$$

$$\mathrm{SO_2Cl_2\ (liq.) + 4Et_2NH\ (liq.) \longrightarrow (Et_2N)_2SO_2\ (diethylamine\ soln.) + 2Et_2NH_2Cl\ (cryst.)} \quad (4)$$

The products of these reactions are diethylammonium chloride, diethylaminotrimethylsilane, *NN'*-dithiodiethylamine, *NN'*-thionylbisdiethylamine, and *NN'*-sulphurylbisdiethylamine. The heats of these reactions have been measured.

EXPERIMENTAL

Compounds.—Cyclohexane and diethylamine were dried over calcium hydride and distilled through an 18-in. Fenske column. Chlorotrimethylsilane, sulphur monochloride, thionyl chloride, and sulphuryl chloride were distilled in an atmosphere of dry nitrogen, through an 18-in. Fenske column. The fractions used had b. p. 56·5°/750 mm. (lit.,[8] 57·3°/760 mm.), 136·0°/752 mm. (lit.,[9] 138·0°/760 mm.), 75·0°/748 mm. (lit.,[9] 78·7°/760 mm.), and 67·9°/744 mm. (lit.,[9] 69·3°/760 mm.), respectively. Diethylaminotrimethylsilane was prepared by the reaction [6] of chlorotrimethylsilane and diethylamine in ether; it was distilled through a 6-in. Fenske column, and had b. p. 126·0°/745 mm. (lit.,[6] 126·1°/750 mm.). *NN'*-Dithiodiethylamine was made by reaction of sulphur monochloride and diethylamine in ether (cf. Birchall and Coffey [10]). The compound, a yellow liquid, could not be distilled at temperatures above 25° without decomposition. *NN'*-Thionylbisdiethylamine was prepared from thionyl chloride and diethylamine by a modification of the method used by Burg and Woodrow [11] for the preparation of *NN'*-thionylbisdimethylamine; it was distilled through a 6-in. Fenske column, and had b. p. 80·0°/0·1 mm. (lit.,[12] 118°/27—28 mm.). Behrend's method [13] was used to prepare *NN'*-sulphurylbisdiethylamine from sulphuryl chloride and diethylamine; the colourless liquid was distilled through a 6-in. Fenske column, having b. p. 89·0°—90·0°/0·1 mm.

Calorimeter.—The heats of reaction were measured in calorimeters which have been described previously.[14,15] The aminolysis of thionyl chloride and sulphuryl chloride were carried out in a cylindrical silvered Dewar vessel (capacity 300 ml.) encased in a brass can; for the reactions of chlorotrimethylsilane and sulphur monochloride a larger, spherical, silvered Dewar vessel (capacity 1 l.) with a long neck was used. Both vessels were immersed in a thermostat-bath at 25·000° ± 0·005°. Temperature measurements were made from the resistance change of a thermistor element. The calorimeter was calibrated electrically by the substitution method. The reactions were carried out by breaking ampoules of the chlorides into diethylamine, liquid or in cyclohexane solution.

[3] Fowell and Mortimer, *J.*, 1959, 2913.
[4] Bedford and Mortimer, *J.*, 1960, 1622.
[5] Claydon, Fowell, and Mortimer, *J.*, 1960, 3284.
[6] Sauer and Hasek, *J. Amer. Chem. Soc.*, 1946, **68**, 243.
[7] Becke-Goehring, University of Heidelberg, personal communication, 1960.
[8] Booth and Shuttle, *J. Amer. Chem. Soc.*, 1946, **68**, 2658.
[9] Dodd and Robinson, "Experimental Inorganic Chemistry," Elsevier, Amsterdam, 1954, pp. 218, 245.
[10] Birchall and Coffey, I.C.I. Ltd., B.P. 331,016/1929.
[11] Burg and Woodrow, *J. Amer. Chem. Soc.*, 1954, **76**, 219.
[12] Michaelis, *Ber.*, 1895, **28**, 1016.
[13] Behrend, *Ber.*, 1882, **15**, 1612.
[14] Pedley, Skinner, and Chernick, *Trans. Faraday Soc.*, 1957, **53**, 1612.
[15] Mortimer and Skinner, *J.*, 1952, 4331.

Units.—Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. J.

Results.—Typical results for the heats of reaction are shown in the Table, in which ΔH_1, ΔH_2, ΔH_3, and ΔH_4 refer to reactions 1, 2, 3, and 4, respectively. In each case the uncertainty associated with ΔH_1, ΔH_2, ΔH_3, and ΔH_4 values is twice the standard deviation of the mean of a number of results, only a selection of which are given in the Table.

Heats of reaction with diethylamine.

Me_3SiCl (g.)	0·4540	0·4788	0·5143	0·5422		
$-\Delta H_1$ (kcal./mole)	33·11	32·55	32·39	32·75		
Mean $\Delta H_1 = -32·7 \pm 0·2$ kcal./mole.						
S_2Cl_2 (g.)	1·2566	0·9229	0·6899	0·5707	0·8439	0·3870
$-\Delta H_2$ (kcal./mole)	87·34	87·15	90·49	89·71	86·14	87·15
Mean $\Delta H_2 = -88·00 \pm 0·7$ kcal./mole.						
$SOCl_2$ (g.)	0·2004	0·2161	0·1671	0·2066	0·1671	0·1435
$-\Delta H_3$ (kcal./mole)	93·14	93·20	94·50	94·82	90·48	97·20
Mean $\Delta H_3 = -93·9 \pm 1·0$ kcal./mole.						
SO_2Cl_2 (g.)	0·2316	0·1216	0·2016	0·1652	0·1951	0·1874
$-\Delta H_4$ (kcal./mole)	132·23	126·70	133·45	126·70	126·95	133·45
Mean $\Delta H_4 = -129·8 \pm 1·7$ kcal./mole.						

The following heats of solution have been measured: in cyclohexane, Et_2NH (liq.), + 0·44 ± 0·03;[3] in cyclohexane–diethylamine, $Me_3Si{\cdot}NEt_2$ (liq.), + 0·29 ± 0·05; $(Et_2N)_2S_2$, + 1·05 ± 0·06; in diethylamine, $(Et_2N)_2SO$ (liq.), − 3·16 ± 0·11; $(Et_2N)_2SO_2$ (liq.), + 0·21 ± 0·06 kcal./mole.

Incorporating these data and the $\Delta H_f°$ values: Et_2NH (liq.), −24·8 ± 0·3;[16] Et_2NH_2Cl (cryst.), −85·76 ± 0·33;[3] S_2Cl_2 (liq.), − 14·4 ± 0·2;[17] $SOCl_2$ (liq.), − 58·45 ± 0·20; and SO_2Cl_2 (liq.), − 93·55 ± 0·20 kcal./mole,[18] the following heats of formation are obtained; $\Delta H_f°[(Et_2N)_2S_2$, liq.$] = -29·4 \pm 1·6$; $\Delta H_f°[(Et_2N)_2SO$, liq.$] = -75·5 \pm 1·7$; and $\Delta H_f°[(Et_2N)_2SO_2$, liq.$] = -149·8 \pm 2·3$ kcal./mole, and the difference $[\Delta H_f°(Me_3SiNEt_2$, liq.$) - \Delta H_f°(Me_3SiCl$, liq.$)] = +4·1 \pm 1·3$ kcal./mole.

DISCUSSION

The difference between the bond energies of the silicon–chlorine and silicon–nitrogen bonds is given by

$$[E(\text{Si–Cl}) - E(\text{Si–N})] = [\Delta H_f°(Me_3Si{\cdot}NEt_2,\text{ g}) - \Delta H_f°(Me_3SiCl,\text{ g})] \\ + \Delta H_f°(\text{Cl,g}) - \textstyle\sum \Delta H_f°(\text{atoms }NEt_2,\text{ g}) + E(NEt_2),$$

where $\sum\Delta H_f°$(atoms NEt_2, g) is the sum of the heats of formation of the atoms comprising the NEt_2 group, and $E(NEt_2)$ is the sum of the bond energies of the NEt_2 group. The $\Delta H_f°$ values are used: C, 170·89; H, 52·09; N, 112·9; Cl, 28·94 kcal./g.-atom,[19] together with $E(NEt_2) = 1293·05$ kcal./mole.[3] The latent heat of vaporisation of chlorotrimethylsilane is 7·22 kcal./mole;[8] that of diethylaminotrimethylsilane is estimated, from its boiling point, as 9·0 ± 0·5 kcal./mole. These results lead to the value $[E(\text{Si–Cl}) - E(\text{Si–N})] = 10·5$ kcal./mole. A value for E(Si–Cl) may be obtained from the relation $E(\text{Si–Cl}) = -\Delta H_f{}^{a}(SiCl_4,\text{ g.})$. By using the values $\Delta H_f°(SiCl_4,\text{ g}) = -149·4 \pm 0·5$

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[16] Prosen, National Bureau of Standards, Washington, D.C., personal communication.

[17] National Bureau of Standards, Circular 500, Washington, D.C., 1952.

[18] Neale and Williams, *J.*, 1954, 2156.

[19] Cottrell, " The Strengths of Chemical Bonds," 2nd edn., Butterworths Scientific Publns., London, 1958.

kcal./mole [20] and $\Delta H_f°(\text{Si, g.}) = 110 \pm 2$ kcal./g.-atom,[21] the value $E(\text{Si–Cl}) = 93{\cdot}8$ kcal.mole is obtained. Hence we derive $E(\text{Si–N}) = 83{\cdot}3$ kcal./mole.

The bond energy E(S–N) may be calculated from the relation

$$E(\text{S–N}) = -\Delta H_f^a[(\text{Et}_2\text{N})_2\text{S}_2,\ \text{g}] - E(\text{NEt}_2) - E(\text{S–S}).$$

The latent heat of vaporisation of *NN'*-dithiodiethylamine has not been measured, but it is reasonable to expect that it will be *ca.* 4 kcal./mole greater than that of sulphur monochloride,[17] *i.e.*, 12·6 kcal./mole. This leads to $\Delta H_f°[(\text{Et}_2\text{N})_2\text{S}_2,\ \text{g}] = -16{\cdot}8 \pm 2{\cdot}0$ kcal./mole. In the alkyl disulphides and the S_8 molecule the sulphur–sulphur bond energy is given [22] by the relation $E(\text{S–S}) = 12{\cdot}7 + \Delta H_f°(\text{S, g})$ kcal./mole. The heat of atomisation of sulphur is controversial, but we take $\Delta H_f°(\text{S, g}) = 66{\cdot}7$ kcal./mole, recommended [23] by Norrish and Oldershaw, by Dewing and Richardson, and also by Mackle and O'Hare. This leads to $E(\text{S–S}) = 79{\cdot}4$ kcal./mole. From these data we calculate $E(\text{S–N}) = 59{\cdot}7$ kcal./mole. This may be compared with $E(\text{S–Cl}) = 58{\cdot}8$ kcal./mole, calculated from the value $\Delta H_f°(\text{S}_2\text{Cl}_2,\ \text{g}) = -5{\cdot}8$ kcal./mole.[17] It is interesting that the difference $[E(\text{A–Cl}) - E(\text{A–N})]$ decreases from 10·5 (A, Si), through 10·0 (A, P)[3] to −0·9 kcal./mole (A, S). This decrease in the strength of the A–Cl bond relative to the A–N bond may be due, in part, to a diminishing amount of d_π–p_π-bonding in the A–Cl bonds, relative to the A–N bonds, along the series A = Si, P, S. In the compounds chlorotrimethylsilane, phosphorus trichloride, and sulphur monochloride the observed [24] bond lengths and those calculated from the sum of the covalent radii [25] (in parentheses) for the A–Cl bonds are Si, 2·03 (2·16); P, 2·00 (2·09); S, 1·99 (2·03) Å. Certainly the bond shortening, which has been attributed to the effect of d_π–p_π-bonding,[2] decreases along the series. Unfortunately, there are insufficient data to compare the bond lengths of the A–N bonds, in diethylaminotrimethylsilane, $\text{Me}_3\text{Si·NEt}_2$, trisdiethylaminophosphine, $(\text{Et}_2\text{N})_3\text{P}$, and *NN'*-dithiodiethylamine, $(\text{Et}_2\text{N})_2\text{S}_2$. However, the A–N bond lengths in the two eight-membered ring systems octamethylcyclotetrasilazane, $[\text{Me}_2\text{SiNH}]_4$,[24] and tetrasulphur tetraimide, $[\text{SNH}]_4$ [26] are: Si, 1·78 (1·91); S, 1·67 (1·78) Å; so that the sulphur–nitrogen bond is shortened to much the same extent (0·11 Å) as the silicon–nitrogen bond (0·13 Å).

The dissociation energies, D(S=O), corresponding to the gas-phase dissociations $\text{R}_2\text{SO}_2 \longrightarrow \text{R}_2\text{SO} + \text{O}$ can be calculated from the relation

$$D(\text{S=O}) = \Delta H_f°(\text{R}_2\text{SO, g}) + \Delta H_f°(\text{O, g}) - \Delta H_f°(\text{R}_2\text{SO}_2,\ \text{g}).$$

Using the heats of formation of liquid thionyl chloride and sulphuryl chloride given above, together with the latent heats of vaporisation of these compounds (7·41 and 7·50 kcal./mole.[17] respectively) and the value $\Delta H_f°(\text{O, g}) = 59{\cdot}54$ kcal./g.-atom,[19] we obtain the value $D(\text{S=O}) = 94{\cdot}6 \pm 0{\cdot}5$ kcal./mole, when R = Cl. The latent heats of vaporisation of *NN'*-thionylbisdiethylamine and *NN'*-sulphurylbisdiethylamine have not been measured. We assume that the latent heat of vaporisation of the sulphuryl derivative is 3·0 ± 0·2 kcal./mole greater than that of the thionyl derivative. The latent heat of vaporisation of *NN'*-sulphurylbisdimethylamine is 2·85 kcal./mole greater than that of *NN'*-thionylbisdimethylamine.[11] Using the values for the heats of formation of these compounds given above, we calculate $D(\text{S=O}) = 130{\cdot}8 \pm 4{\cdot}2$ kcal./mole, where $\text{R} = \text{Et}_2\text{N}$.

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[20] Flitcroft and Skinner, *J.*, 1956, 3355; Roth and Schwartz, *Z. phys. Chem.*, 1928, **134**, 456.

[21] Sinke, Dow Chemical Company, Midland, Michigan, personal communication.

[22] Good, Lacina, and McCullough, *J. Phys. Chem.*, 1961, **65**, 860; Hubbard, Douslin, McCullough, Scott, Todd, Messerly, Hossenlop, George, and Waddington, *J. Amer. Chem. Soc.*, 1958, **80**, 3547.

[23] Norrish and Oldershaw, *Proc. Roy. Soc.*, 1959, *A*, 249, 498; Dewing and Richardson, *Trans. Faraday Soc.*, 1958, **54**, 679; Mackle and O'Hare, *ibid.*, 1961, **57**, 1070.

[24] "Interatomic Distances," *Chem. Soc. Special Publ.* No. 11, 1958.

[25] Moeller, " Inorganic Chemistry," Chapman and Hall, London, 1952.

[26] Sass and Donohue, *Acta Cryst.*, 1958, **11**, 497; Lund and Svendsen, *Acta Chem. Scand.*, 1957, **11**, 940.

The heat of oxidation of dimethyl sulphoxide to dimethyl sulphone in permanganate solution, at 18°, has been measured directly.[27] A value of $\Delta H = -59{\cdot}0 \pm 0{\cdot}2$ kcal./mole was obtained for the reaction

$$\mathrm{Me_2SO(liq.)} + \mathrm{O_2(g)} \longrightarrow \mathrm{Me_2SO_2(cryst.)}$$

The latent heat of vaporisation of dimethyl sulphoxide has been given as $\Delta H_{\text{vap.}} = 12{\cdot}64$ kcal./mole,[17] and the latent heat of sublimation of dimethyl sulphone has been measured as $\Delta H_{\text{sub.}} = 18{\cdot}4 \pm 0{\cdot}9$ kcal./mole.[28] Using these data we calculate $D(\mathrm{S{=}O}) = 112{\cdot}7 \pm 1{\cdot}3$ kcal./mole, where R = Me.

Thus, for the series R = Cl, $\mathrm{Et_2N}$, Me, we have values for $D(\mathrm{S{=}O})$ of $94{\cdot}6 \pm 0{\cdot}5$, $130{\cdot}8 \pm 4{\cdot}2$, and $112{\cdot}7 \pm 1{\cdot}3$ kcal./mole. In the phosphoryl compounds, $\mathrm{R_3PO}$, we have values for $D(\mathrm{P{=}O})$ in the series R = Cl, $\mathrm{Et_2N}$, Me, of $127{\cdot}5 \pm 0{\cdot}5$,[29] $156{\cdot}0 \pm 3{\cdot}5$, and $139{\cdot}3 \pm 3{\cdot}0$ kcal./mole.[5] These have been calculated from the heats of formation of the gaseous compounds $\mathrm{R_3PO}$ and $\mathrm{R_3P}$. The dissociation energy for the case R = $\mathrm{Et_2N}$ is derived from the heats of formation $\Delta H_f°[(\mathrm{Et_2N})_3\mathrm{PO}, \mathrm{g}] = -148{\cdot}8 \pm 0{\cdot}9$ kcal./mole[30] and $\Delta H_f°[(\mathrm{Et_2N})_3\mathrm{P}, \mathrm{g}] = -52{\cdot}3 \pm 3{\cdot}6$ kcal./mole.[3] It is interesting that, where R = $\mathrm{NEt_2}$, values for both $D(\mathrm{S{=}O})$ and $D(\mathrm{P{=}O})$ are considerably greater than where R = Me or Cl.

It has been suggested[29] that d_π–p_π-bonding, or back co-ordination from the R groups to the phosphorus atom, is increased in $\mathrm{R_3P{=}O}$, as compared with $\mathrm{R_3P}$, causing a strengthening of the P–R bonds in the phosphoryl compounds, which will be included in the dissociation energy $D(\mathrm{P{=}O})$. This effect is likely to be at a maximum for R = $\mathrm{NEt_2}$, because the nitrogen atom has a stronger donor tendency than either the chlorine or carbon atoms. Likewise, it is probable that d_π–p_π-bonding in $\mathrm{R_2SO_2}$ will be greater than in $\mathrm{R_2SO}$, and a maximum value for $D(\mathrm{S{=}O})$ is to be expected for R = $\mathrm{NEt_2}$. This conclusion is supported by measurements[11] of the strength of the nitrogen–boron co-ordinate link in the molecular-addition compounds $(\mathrm{Me_2N})_2\mathrm{SO,BF_3}$ and $(\mathrm{Me_2N})_2\mathrm{SO_2,BF_3}$. The $\mathrm{N} \longrightarrow \mathrm{B}$ bond is much weaker in the latter than in the former compound. Burg and Woodrow[11] attribute the weaker nitrogen–boron bond in the compound $(\mathrm{Me_2N})_2\mathrm{SO_2,BF_3}$ to the effect of the sulphur atom's becoming more electronegative when two oxygen atoms are bonded to it, than when there is a single oxygen atom. This makes for increased d_π–p_π-bonding between the nitrogen and the sulphur atom in the sulphuryl derivative, compared with the thionyl addition compound, which consequently decreases the external donor power of the nitrogen atom.

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[27] Douglas, *J. Amer. Chem. Soc.*, 1946, **68**, 1072.
[28] Busfield, Ivin, Mackle, and O'Hare, *Trans. Faraday Soc.*, 1961, **51**, 1058.
[29] Mortimer, *Pure Appl. Chem.*, 1961, **2**, 71.
[30] Keavney, American Cyanamid Company, Stamford, Conn., personal communication.