The Heat of Formation of the Methylthio-, Ethylthio-, Phenylthio-, and Phenoxy-radicals

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WITH a view to assessing the reliability of the available thermochemical data for the key methylthio-, ethylthio-, phenylthio-, and phenoxy-radicals, we have selected a series of analogous oxygen and sulphur compounds and evaluated the dissociation energies of the bonds involving the oxygen and sulphur atoms.

For ΔH_f° (Ph·) we have adopted a recently determined[1] value of 80 ± 1 kcal./mole, although it is significantly higher (5—10 kcal./mole) than was previously assigned.[2,3] For PhO·, the value of ΔH_f° is calculated to be $10 < \Delta H_f^\circ \leqslant 17$ kcal./mole by combining the ionization potential[4] of the PhO· radical with the appearance potential of the PhO^+ ion from methyl phenyl ether[4] and by using more precise values of ΔH_f° for methyl phenyl ether[5,6] and the methyl radical.[2] Natalis and Franklin[7] suggested a value for ΔH_f° (PhO·) = 9 kcal./mole, but due to an arithmetic inconsistency in their calculations little advantage can be gained from updating their results with later more precise data.[5,8] In agreement with Benson[9] and Gray[10] we have taken ΔH_f° (PhO·) = 13 ± 5 kcal./mole. There is still considerable doubt concerning the heats of formation of the HS·, MeS·, EtS·, and PhS· radicals, and in place of more reliable data we use the literature[2,11] values: ΔH_f° (HS·) = 33 ± 3, ΔH_f° (MeS·) = 29 ± 5, ΔH_f° (EtS·) = 26 ± 5 and ΔH_f° (PhS·) = 50 ± 5 kcal./mole. The heats of formation of Me·, Et·, $PhCH_2$·, ·OH, and MeO· radicals are

Bond-dissociation energies (kcal./mole) in RSR and ROR compounds

R	R–SH	R–OH	R–SPh	R–OPh	R–SMe	R–OMe	R–SEt	R–OEt
H	90	119	75	89	88	102	88	104
Ph	86	112	74	86	87	101	87	103
Me	73	91	60[a]	67	73	79	73	82
Et	70	91	57	66	70	80	71	82
$PhCH_2$	56	79	—	—	55	66[b]	58	—

[a] Determined directly as a route to ΔH_f° (PhS·); [b] estimated value, ref. 20.

taken from Kerr's review[2] and we use Thynne and Leggett's[12] recent value for the ethoxy-radical, ΔH_f° (EtO·) = $-4{\cdot}4 \pm 1$ kcal./mole. Except for diphenyl ether,[13,14] the data for the gas-phase heats of formation of the parent sulphur and oxygen compounds are taken from review articles.[5,14,15]

The bond dissociation energies calculated from these data are listed in the Table.

Pyrolysis experiments on assymmetrical R^1SR^2 and R^1OR^2 compounds offer a test of the validity of comparative bond-dissociation energies. Pyrolyses of methyl phenyl ether,[16] methyl phenyl sulphide,[17] methanethiol,[18] ethanethiol,[18] benzenethiol,[18] and 2-methylpropane-2-thiol[19] give products which are consistent with the initial rupture of the bonds predicted to be the weakest in these molecules.

Primary factors which influence bond-dissociation energies are the nature of the bonded elements, the reorganization which accompanying bond fission, and hybridization or conjugation in the parent compound or the associated free-radicals. In analogous molecules, the dissociation energies involving sulphur atoms are always considerably lower than for those involving oxygen atoms. This is probably due to a smaller σ-bond energy term for the sulphur-containing molecules. The difference between the bond-dissociation energies involving the ethylthio- and methylthio-radicals are almost the same (± 1 kcal./mole) as the difference between the bond-dissociation energies involving the ethoxy- and methoxy-radicals (Table). Similar comparisons can be made for the phenylthio- and phenoxy-radicals.

The data in the Table appear to be self-consistent. Since the bond-dissociation energies are derived from independent measurements for the heat of formation of the radicals combined with independent heat of combustion data, it would seem that previous authors have over-estimated the possible uncertainties. We conclude that the heats of formation of the methylthio-, ethylthio-, phenylthio-, and phenoxy-radicals are not likely to be in error by more than ± 3 kcal./mole.

(*Received, January 7th*, 1968; *Com.* 015.)

[1] A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 1967, **89**, 4578.

[2] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465.

[3] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 1959, **5**, 166; 1960, **11**, 96.

[4] I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, 1964, **86**, 2741.

[5] J. H. S. Green, *Quart. Rev.*, 1961, **15**, 125.

[6] M. M. Badoche, *Bull. Soc. chim. France*, 1941, **8**, 212.

[7] P. Natalis and J. L. Franklin, *J. Phys. Chem.*, 1965, **69**, 2943.

[8] G. P. Adams, D. H. Fine, P. Gray, and P. G. Laye, *J. Chem. Soc. (B)*, 1967, 720.

[9] S. W. Benson, *J. Amer. Chem. Soc.*, 1965, **87**, 972.

[10] Peter Gray, personal communication, 1968.

[11] H. Mackle, *Tetrahedron*, 1963, **19**, 1159.

[12] C. Leggett and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2504.

[13] G. T. Furukawa, D. C. Ginnings, R. E. McCoskey, and R. A. Nelson, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 195.

[14] D. R. Stull, *Ind. and Eng. Chem.*, 1947, **39**, 517.

[15] H. Mackle and P. A. G. O'Hare, *Tetrahedron*, 1963, **19**, 961.

[16] Yu. K. Shaposhnikov and L. V. Kosyukova, *Khim. Pererabotka Drevesing.*, Ref. Inform no. 3, 1965 6–9 (*Chem. Abs*, 1967, **66**, 37557a).

[17] M. H. Back and A. H. Sehon, *Canad. J. Chem.*, 1960, **38**, 1076.

[18] A. H. Sehon and B. deB. Darwent, *J. Amer. Chem. Soc.*, 1956, **76**, 4806.

[19] C. J. Thompson, R. A. Meyer, and J. S. Ball, *J. Amer. Chem. Soc.*, 1952, **74**, 3287.

[20] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.