

[CONTRIBUTION FROM THE REFINING TECHNICAL AND RESEARCH DIVISIONS, HUMBLE OIL & REFINING COMPANY]

Some C-S, H-S and S-S Bond Strengths by the Electron Impact Method

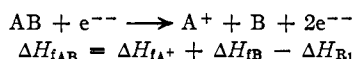
BY J. L. FRANKLIN AND H. E. LUMPKIN

The heats of formation of the $\dot{S}H$, $CH_3\dot{S}$, and $C_2H_5\dot{S}$ radicals have been determined by the method of electron impact to be 38.4, 33.0, and 25.0 kcal./mole, respectively. From this and known thermodynamic data several C-S, H-S, and S-S bond strengths in alkyl sulfur compounds have been calculated. The appearance potentials of the CH_3S^+ and the $C_2H_5S^+$ ions have been measured. The heats of formation have been calculated to be 222.2 and 212.8 kcal./mole, respectively. The heats of combustion of *t*-butyl mercaptan, dimethyl disulfide and diethyl disulfide have been determined approximately.

Introduction

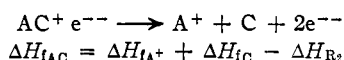
The literature contains very few data concerning bond strengths in organic sulfur compounds. In view of the importance of organic sulfur chemistry, this study was conducted for the purpose of developing information concerning bond strengths in mercaptans, thioethers and disulfides.

In this study the method of electron impact was employed. The method and its limitations have been discussed by Stevenson,¹ Hagstrum,² Szwarc,³ and others and will not be reviewed here, except to give a brief outline of the procedure. If a molecule, AB, is subjected to electron bombardment, it is possible to determine the appearance potential of the fragment A^+ , that is, the lowest voltage at which the A^+ ion is just detectable in the mass spectrometer. If we assume that the energy of the two free electrons remaining after collision is zero, we may write the following thermochemical equation.

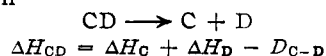


where ΔH_{R1} is the heat of the reaction as calculated from the appearance potential of A^+ . For these purposes energy is given to sufficiently good approximation by ΔH . If the heat of formation of the fragment B, which may be an atom or free radical, is known, the heat of formation of the ion can be calculated. Heats of formation and dissociation energies calculated by this method will tend to be high since ionization by electron impact must be vertical in accordance with the Frank-Condon principle. In practice the results usually agree well with those of other methods, however.

We may again determine the appearance potential of A^+ from a compound AC and, with ΔH_{iA^+} known, this will permit us to calculate the heat of formation of the unchanged fragment or radical, C, thus



Now if we have a compound, CD, we may write the equation



If we know the heat of formation of CD and of the radicals C and D, the heat of the reaction, D_{C-D} , is readily calculated. This is the bond strength.

Discussion

The above sequence of steps was employed in this study for the determination of the strengths of

the S-H, C-S and S-S bonds in several alkyl mercaptans, thioethers and disulfides as well as in H_2S and H_2S_2 . For this purpose it was necessary to know the heats of formation of the $\dot{S}H$ and certain $RS\dot{S}$ free radicals as well as that of several alkyl free radicals. Fortunately, the literature contains values for the heat of formation for a number of alkyl radicals⁴ and consequently this study resolves itself into the determination of the heats of formation of the $\dot{S}H$, $CH_3\dot{S}$ and the $C_2H_5\dot{S}$ radicals.

The $\dot{S}H$ Radical.—In determining the heat of formation of the $\dot{S}H$ radical the appearance potentials of several alkyl carbonium ions were measured when charging alkyl mercaptans to the mass spectrometer. The literature reports many examples of the appearance potentials of alkyl carbonium ions which permit calculation of the heat of formation of the ions. Most of these values were obtained when charging a hydrocarbon or an alkyl halide to the mass spectrometer. Table I gives the heats of formation of several ions as calculated from the data of Stevenson and Hipple.⁵

TABLE I
HEATS OF FORMATION OF GASEOUS IONS

Ion	ΔH_f° , kcal./mole		Parent compound
	S. & H.	This paper	
CH_3^+	261	...	CH_4
$C_2H_5^+$	223	...	C_2H_6
<i>n</i> - $C_3H_7^+$	197	...	<i>n</i> - C_3H_7Cl
<i>i</i> - $C_3H_7^+$	187	...	<i>i</i> - C_4H_{10}
<i>t</i> - $C_4H_9^+$	165	168	<i>t</i> - C_4H_9Cl

Table V gives the appearance potentials of the ethyl, *n*-propyl and *t*-butyl ions determined in this study by electron bombardment of the corresponding mercaptan. The heat of formation of the $\dot{S}H$ radical calculated from these values is given in Table II. It will be observed that the average

TABLE II
HEATS OF FORMATION OF $\dot{S}H$, $CH_3\dot{S}$ AND $C_2H_5\dot{S}$

	ΔH_f° of ion, kcal./mole	ΔH_f° of radical, kcal./mole	
		From	From
$\dot{S}H$		36.9	$C_2H_5\dot{S}H$
$\dot{S}H$		44.4	<i>n</i> - $C_3H_7\dot{S}H$
$\dot{S}H$		33.9	<i>t</i> - $C_4H_9\dot{S}H$
Average		38.4	
$CH_3\dot{S}$	222.2	$(CH_3)_2\dot{S}$	$(CH_3)_2S_2$
$C_2H_5\dot{S}$	212.8	$(C_2H_5)_2\dot{S}$	$(C_2H_5)_2S_2$

(4) J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

(5) D. P. Stevenson and J. A. Hipple, *THIS JOURNAL*, **64**, 1588, 2766 (1942); Hipple and Stevenson, *Phys. Rev.*, **63**, 121 (1943).

(1) D. P. Stevenson, *J. Chem. Phys.*, **10**, 291 (1942).

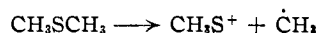
(2) H. D. Hagstrum, *Phys. Rev.*, **72**, 947 (1947).

(3) M. Szwarc, *Quarterly Rev., Chem. Soc.*, **5**, 22 (1951).

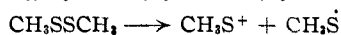
value of the heat of formation of the $\dot{\text{S}}\text{H}$ radical is 38.4 kcal./mole. The uncertainty, which is approximately ± 5 kcal./mole, is greater than we like, but is probably little greater than is to be expected for this method. It would have been interesting to determine the appearance potential of H^+ from H_2S but instrument limitations made this impossible.

The heats of formation of the methyl and ethyl ions used in these calculations were taken from Table I. Our value (168 kcal./mole) for the heat of formation of the *t*-butyl ion differed slightly from that of Stevenson and Hipple⁴ and was used in these calculations since the fact that it was obtained on the same instrument as other values measured in this study should make the results somewhat more accurate. In calculating the heat of formation of the $\dot{\text{S}}\text{H}$ radical we employed Barrow and Pitzer's⁶ values of the heats of formation of ethyl and *n*-propyl mercaptans. Values were not available for the *t*-butyl mercaptan and accordingly it was necessary to measure the heat of combustion of this compound. The heat of formation of gaseous *t*-butyl mercaptan determined in this way was -27.8 kcal./mole as shown in Table VI.

The $\text{CH}_3\dot{\text{S}}$ and $\text{C}_2\text{H}_5\dot{\text{S}}$ Radicals.—In order to determine the heat of formation of the $\text{CH}_3\dot{\text{S}}$ and $\text{C}_2\text{H}_5\dot{\text{S}}$ radicals it would be convenient to measure the appearance potential of the methyl or ethyl ions when charging dimethyl or diethyl thioethers. These measurements were made but, as will be discussed later, the results gave values for the bond strengths that were not reasonable. Accordingly, a somewhat different procedure was employed. The appearance potentials of the CH_3S^+ and the $\text{C}_2\text{H}_5\text{S}^+$ ions from the corresponding thioethers were measured and this permitted the heats of formation of these ions to be calculated since ΔH_f values for the methyl and ethyl radicals are known. The appearance potentials of these ions were then measured when charging $(\text{CH}_3)_2\text{S}_2$ and $(\text{C}_2\text{H}_5)_2\text{S}_2$. As can be seen from the following equations, the heats of formation of the radicals are readily determined in this way. However, since no heats of formation of disulfides were available, it was necessary to measure the heats of combustion of CH_3SSCH_3 and $\text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$. These results are given in Table VI.



$$\Delta H_{\text{CH}_3\text{SCH}_3} = \Delta H_{\text{CH}_3\text{S}^+} + \Delta H_{\dot{\text{C}}\text{H}_3} - \Delta H_{\text{R}_1}$$



$$\Delta H_{\text{CH}_3\text{SSCH}_3} = \Delta H_{\text{CH}_3\text{S}^+} + \Delta H_{\text{CH}_3\dot{\text{S}}} - \Delta H_{\text{R}_2}$$

where ΔH_{R_1} and ΔH_{R_2} are the appearance potentials converted to kcal. The heat of formation of the $\text{C}_2\text{H}_5\dot{\text{S}}$ radical can be similarly determined. Table II gives the values for the heats of formation of the ions and radicals thus determined.

Bond Strengths.—From the heats of formation of the various radicals, as measured in this study and known values for various alkyl radicals, a number of C-S bond strengths have been determined. Table III gives values for the C-S bond

strengths in several mercaptans and thioethers as well as in the $\text{CH}_3\dot{\text{S}}$ and $\text{C}_2\text{H}_5\dot{\text{S}}$ radicals. In calculating these bond strengths, the heats of formation of the alkyl radicals were taken from Roberts and Skinner.⁴ The heats of formation of the methyl, ethyl, *n*-propyl and *t*-butyl mercaptans were known as were those of dimethyl and diethyl thioethers. Heats of formation of all other parent compounds were estimated by the method of group equivalents.⁷ The strength of the C-S bonds varies but little with the second group attached to the sulfur, being substantially the same whether a hydrogen, a methyl or an ethyl group is attached to the sulfide. Indeed, it is perhaps doubtful whether the variation shown is significant.

TABLE III
CARBON-SULFUR BOND STRENGTHS IN ALIPHATIC THIOALS AND THIO ETHERS (KCAL./MOLE)

R	$\Delta H_{\text{R}^{\cdot}}$	$D_{(\text{R}-\text{SH})}$	$D_{(\text{R}-\text{SCH}_3)}$	$D_{(\text{CH}_3-\text{S})}$	$D_{(\text{R}-\text{SC}_2\text{H}_5)}$	$D_{(\text{C}_2\text{H}_5-\text{S}\cdot)}$
CH_3	32.1	74.2	73.2	52.4	70.6	..
C_2H_5	25.3	73.4	71.8	..	69.3	53.6
<i>n</i> - C_3H_7	18.7	72.1	69.7	..	67.7	..
<i>i</i> - C_3H_7	14.0	70.6	67.0	..	65.0	..
<i>t</i> - C_4H_9	3.2	69.4	65.2	..	62.2	..
Allyl	30.9	54.3	51.9	..	49.9	..

The S-H and S-S bond dissociation energies in several compounds are given in Table IV. In calculating these values the heats of formation of H_2S , H_2S_2 , H, S_2 and S were taken from reference 8. The heats of formation of methyl and ethyl mercaptans were taken from Barrow and Pitzer.⁶ The heats of formation of methyl disulfide and ethyl disulfide were determined in this study from heats of combustion and that of methyl ethyl disulfide was estimated by the method of group equivalents.⁷

TABLE IV
SOME S-H AND S-S BOND STRENGTHS

Compound	Bond	Bond strength, kcal./mole
H_2S	H-SH	95.3
	S-H	67.0
CH_3SH	$\text{CH}_3\text{S-H}$	88.8
$\text{C}_2\text{H}_5\text{SH}$	$\text{C}_2\text{H}_5\text{S-H}$	86.8
S_2	S-S	76, 81, 101
H_2S_2	HS-SH	80.4
CH_3SSCH_3	$\text{CH}_3\text{S-SCH}_3$	73.2
$\text{CH}_3\text{SSC}_2\text{H}_5$	$\text{CH}_3\text{S-SC}_2\text{H}_5$	71.5
$\text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{S-SC}_2\text{H}_5$	70.0

The difference in the strength of the first and second S-H bonds in H_2S is somewhat greater than would be expected but is qualitatively similar to that found for the first and second O-H bonds in water (117.8 and 101 kcal./mole, respectively⁹). On the basis of spectroscopic evidence, Porter¹⁰ found the dissociation energy of SH to be 84.9 kcal./mole. If this value is correct then $D_{\text{R-SH}}$

(7) J. L. Franklin, *ibid.*, **41**, 1070 (1949).

(8) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., June 30, 1949.

(9) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1947, pp. 212, 219.

(10) G. Porter, *Discussions of the Faraday Soc.*, **9**, 60 (1950).

(6) G. M. Barrow and K. S. Pitzer, *Ind. Eng. Chem.*, **41**, 2737 (1949).

is 77.4 kcal./mole; that is, the first bond is weaker than the second in H_2S . Although this presumably is not impossible, it is contrary to what is usually found and so we are inclined to prefer our values of the S-H bond strengths in H_2S to those of Porter.

The dissociation energy of S_2 has been in doubt for some time, the principal values under consideration being 76, 81 and 101 kcal./mole¹¹ as shown in Table IV. Since the bond in S_2 is a double bond,¹² one would expect it to be somewhat stronger than the single S-S bond in H_2S_2 . However, the difference in bond strength between the single and double bonds joining elements of the second period of the periodic table should be considerably smaller than the corresponding difference in bond strengths between elements of the first period. The difference between the O-O bond in O_2 and in H_2O_2 is 67 kcal./mole⁹ and we would expect the difference in the S-S bond in S_2 and H_2S_2 to be considerably smaller than this. On this basis then, the higher value for D_{S-S} , namely, 101 kcal./mole, appears to be the correct one.

It is interesting that the strengths of the S-S bonds in the alkyl disulfide are about the same as that of the C-S bonds in mercaptans and thioethers. Although we do not have data to permit calculation of the C-S bonds in the disulfides, one would be rather surprised if these were far different. The strength of the S-S bonds in trisulfides and higher polysulfides is not known, but one would expect them to be only slightly weaker than the S-S bond in the disulfides. The ease with which trisulfides are produced by the addition of sulfur to disulfides tends to bear this out. It is noteworthy that the strength of the S-S bond in disulfides is in the neighborhood of 70 kcal./mole, whereas that of the O-O bond in di-*t*-butyl peroxide is 39 kcal./mole.¹³ With this and the fact that the strength of the O-H bond in *t*-butanol is 105 kcal./mole whereas the S-H bond in mercaptans is about 85 kcal./mole, it is not surprising that mercaptans are readily oxidized to disulfides whereas alcohols are not oxidized to peroxides. The difference in the O-O and S-S bond strengths is also reflected in the greater thermal stability of the disulfides as compared to the peroxides.

Appearance Potentials of the CH_3^+ and $C_2H_5^+$ Ions in Dimethyl and Diethyl Thioethers.—It will be recalled that attempts to determine the heats of formation of the $CH_3\dot{S}$ and $C_2H_5\dot{S}$ radicals by measuring the appearance potential of the methyl and ethyl ions from the dimethyl and diethyl thioethers, respectively, gave values resulting in abnormally high bond strengths. The heats of formation of these assumed radicals and the CH_3S-CH_3 and $C_2H_5S-C_2H_5$ bond strengths, as calculated from the appearance potentials in Table V, are given.

Calcd. ΔH_f of radicals, kcal./mole		Bond strengths, kcal./mole	
$CH_3\dot{S}$	81.4	CH_3S-CH_3	121.6
$C_2H_5\dot{S}$	52.2	$C_2H_5S-C_2H_5$	96.2

(11) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 194.

(12) L. R. Maxwell, V. M. Mosley and S. B. Hendricks, *Phys. Rev.*, **50**, 41 (1936).

(13) F. H. Seubold, F. D. Rust and W. E. Vaughan, Paper 25, Org. Div. A. C. S. Meeting No. 118, Chicago, Ill., 1950.

These values are far higher than is reasonable. The manner in which these compounds decomposed when forming the methyl and ethyl ions is a matter of some interest and several reactions were considered in speculating as to the manner in which the molecules break down. If it is assumed that the dimethyl thioether breaks down to give a methyl radical and a sulfur atom as well as the methyl ion, quite close agreement with the experimental value for the appearance potential is found. The calculated and observed values are, respectively, 354.5 and 350.5 kcal./mole.

If the diethyl thioether is assumed to break down in an analogous fashion to give the ethyl radical, a sulfur atom and an ethyl ion, the agreement with the experimental data is quite poor, the discrepancy being in the order of one electron volt. If, however, the molecule is assumed to decompose to ethylene, the $\dot{S}H$ radical and $C_2H_5^+$, we find excellent agreement with the measured value. The calculated and observed values are 292.9 and 294.2 kcal./mole, respectively. It seems rather probable therefore for higher thioethers the tendency would be to form the olefin and the $\dot{S}H$ radical rather than the sulfur and the alkyl radical.

Experimental

Appearance Potential Measurements.—All appearance potential measurements are made on a Westinghouse Type LV mass spectrometer, which employs a 90° tube. The electrons are emitted from a hot tungsten filament and accelerated to the ionization chamber by a first and second electron slit at 10 and 40 volts above the filament voltage, respectively. The energy of the electrons entering the ionization chamber is controlled by two 3600° wire wound helipot acting as coarse and fine controls and measured on a Leeds and Northrup Type K-2 potentiometer. In conjunction with a Leeds and Northrup No. 7591 voltage divider, the potentiometer will measure absolute voltages to better than +0.1%. The potentiometer, voltage divider and table galvanometer are high voltage insulated to permit safe operation. A cross-field pusher potential of 0.5 volt is employed. Ion currents are measured with a Leeds and Northrup light beam galvanometer with a millimeter scale placed one meter from the galvanometer. A Julius suspension is employed for galvanometer stability. Deflections of one millimeter, corresponding to 6×10^{-16} ampere, can be detected.

The calibrating gas, krypton in all cases, is introduced simultaneously with the unknown and the ion currents at 75 electron volts for the krypton ion and the ion under investigation are made equivalent at $1-3 \times 10^{-12}$ ampere. Measurements are taken beginning about one to two volts above the appearance potential and reducing the ionizing voltage in 0.02 to 0.06 volt steps. In general a magnetic current of 48 ma. is used and the peaks focused by varying the ion acceleration voltage. Mass 84 is in focus at 328 volts. The appearance potential values quoted below and employed in the subsequent calculation are the average of duplicate or triplicate determinations on one to three samples. The vanishing current method of Smyth¹⁴ is employed. All values are based on the spectroscopic ionization potential for krypton of 14.00 electron volts, computed from the data of Bacher and Goudsmit¹⁵ employing the new accepted conversion factor 8068.2 $cm^{-1} = 1$ electron-volt. The conversion factor employed for interconverting molecular and molar energy units is 1 abs. electron-volt/molecule $\times 23.063 = 1$ kcal./mole.

In order to ascertain the accuracy of the method, values for the ionization potentials of carbon dioxide, ethane and ethylene were measured. The literature contains rather satisfactory values for all of these compounds and our results

(14) H. D. Smyth, *Phys. Rev.*, **25**, 452 (1925).

(15) R. F. Bacher and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., Inc., New York, N. Y., 1932, p. 251.

TABLE V
 APPEARANCE POTENTIALS OBTAINED IN THIS STUDY AND COMPARISON WITH VALUES OF OTHERS

Compound	Source and purity	Ion	Appearance potential, e.v.	Spec.	Literature values, e.v.		Ref.
					Electron	Impact	
Krypton	100 mole % ^a	Kr ⁺	Standard	14.00		15	
Carbon dioxide	99.956 ^a	CO ₂ ⁺	13.78	13.79		16	13.85
Ethane	99.75 ^b	C ₂ H ₆ ⁺	11.60				11.59
Ethylene	100 ^b	C ₂ H ₄ ⁺	10.46	10.51		17	10.62
<i>t</i> -Butyl chloride ^c		<i>t</i> -C ₄ H ₉ ⁺	10.38				10.27
Ethyl mercaptan	99.95 ^d	C ₂ H ₅ ⁺	11.69				
<i>n</i> -Propyl mercaptan ^c		<i>n</i> -C ₃ H ₇ ⁺	11.12				
<i>t</i> -Butyl mercaptan	99.92 ^d	<i>t</i> -C ₄ H ₉ ⁺	9.96				
Methyl sulfide		CH ₃ ⁺	15.2				
		CH ₃ S ⁺	11.38				
Ethyl sulfide	99.94 ^d	C ₂ H ₅ ⁺	12.76				
		C ₂ H ₅ S ⁺	11.15				
Methyl disulfide		CH ₃ S ⁺	11.38				
Ethyl disulfide	99.90 ^d	C ₂ H ₅ S ⁺	11.18				

^a The Matheson Co. ^b Phillips Petroleum Co. ^c Eastman Kodak Co. White Label. ^d National Bureau of Standards.

are compared with both spectroscopic and electron impact measurements on these compounds in Table V. The agreement is excellent in all cases. Table V also gives all of the appearance potentials measured in this study.

Heats of Combustion.—Since the literature contains relatively little information concerning the heats of combustion of sulfur compounds, it has been necessary in a few instances to determine the heats of combustion in this laboratory. For this purpose, we employed ASTM Test D-240 for determining heat of combustion as modified by Jones and Starr.¹⁹ In these experiments no water was added to the bomb. When calculating the heat of formation of the compound it was assumed that all of the sulfur went to H₂SO₄ and the heat of formation of the sulfuric acid was taken as that of sulfuric acid diluted with the number of moles of water formed during combustion. Heats of combustion of thiophene, *t*-butyl mercaptan, dimethyl disulfide and diethyl disulfide have been determined. Table VI gives the heats of combustion and the calculated heats of formation of the compounds. Our values of 19.2 for the heat of formation of thiophene is compared with Moore, Renquist and Parks'²⁰ value of 19.62 kcal./mole. The agreement is probably better than would be realized consistently. The precision, while not as good as would be desired for very exact work, is probably sufficiently close for the present purpose in view of the inaccuracies in the measurement of appearance potentials.

The heats of vaporization were taken from the reports of API Research Project 48A,²¹ except for that of diethyl di-

 TABLE VI
 HEATS OF COMBUSTION AND HEATS OF FORMATION OF SEVERAL COMPOUNDS

	Heat of comb., kcal./mole	$\Delta H_f(l)$, kcal./mole	$\Delta H_f(g)$, kcal./mole
Thiophene	665.0 665.2 662.8		
Average	664.3	19.2	27.5
<i>t</i> -C ₄ H ₉ SH	822.0 821.3		
Average	821.7	-34.6	-27.8
CH ₃ -S-S-CH ₃	632.0 632.0 636.3		
Average	635.4	-16.4	-7.2
C ₂ H ₅ -S-S-C ₂ H ₅	953.7 954.4		
Average	954.05	-32.5	-20.0

sulfide which was estimated from values for other compounds.

Acknowledgments.—We wish to express our appreciation to Messrs. J. H. Karchmer and J. E. McDaniel for their work in carrying out the heats of combustion and to Mr. T. P. Gorman for his assistance in preparing the mass spectrometer for these studies. We wish also to thank Humble Oil & Refining Company for permission to publish these results.

BAYTOWN, TEXAS

RECEIVED JULY 19, 1951

(16) W. C. Price and D. M. Simpson, *Proc. Roy. Soc. (London)*, **A169**, 501 (1939).

(17) W. C. Price and W. T. Tutte, *ibid.*, **A174**, 207 (1940).

(18) R. E. Honig, *J. Chem. Phys.*, **16**, 105 (1948).

(19) W. H. Jones and C. E. Starr, *Ind. Eng. Chem., Anal. Ed.*, **13**, 287 (1941).

(20) G. E. Moore, M. L. Renquist and G. S. Parks, *THIS JOURNAL*, **62**, 1505 (1940).

(21) "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," Third Annual Report, October 1, 1950, Table VIII, Research Project 48A, American Petroleum Institute.