A small drop of the dye mixture (dissolved in the solvent system used) was placed at the apex of the strips and after the ascending solvent fronts had coalesced at the apex, a potential was applied across the strips by means of platinum electrodes immersed in the electrode vessels.

Figure 1 was prepared from a tracing of paper strips and illustrates the separation of an electropositive dye (crystal violet) and an electronegative dye (Oil Red O). In this separation a mixture of nitromethane (9 vol.) and glacial acetic acid (1 vol). was used. Similar separations have been effected in absolute ethyl alcohol, methanol and in pyridine–glacial acetic acid mixtures.[5] Included in Fig. 1 is an ascending chromatogram[6] in the same nitromethane–glacial acetic acid solvent where it will be noted no separation was achieved.

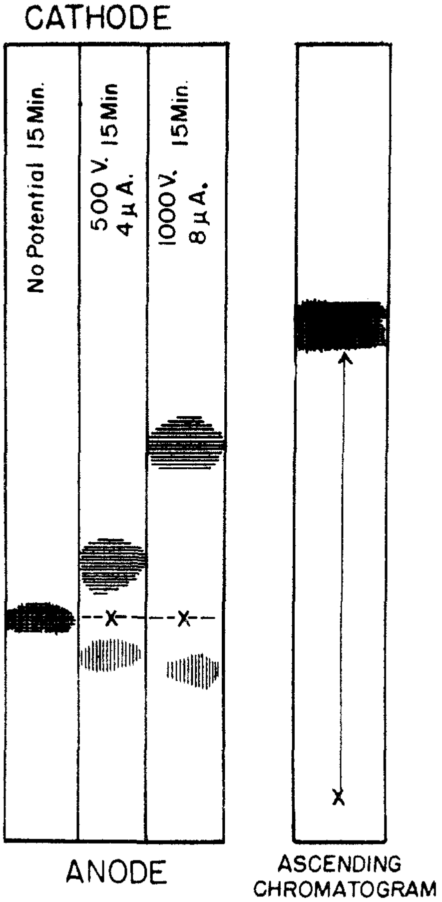

Fig. 1.—Separation of oil red O (vertical lines) and crystal violet (horizontal lines) in nitromethane–glacial acetic acid mixture.

In Fig. 2 the separation of a mixture of four dyes in absolute ethyl alcohol is illustrated.

Cholesterol, palmitic acid, 17-hydroxy-11-dehydrocorticosterone and testosterone were found to migrate toward the anode in the ethyl alcohol or nitromethane–glacial acetic acid systems; however, no separation of these mixtures of compounds

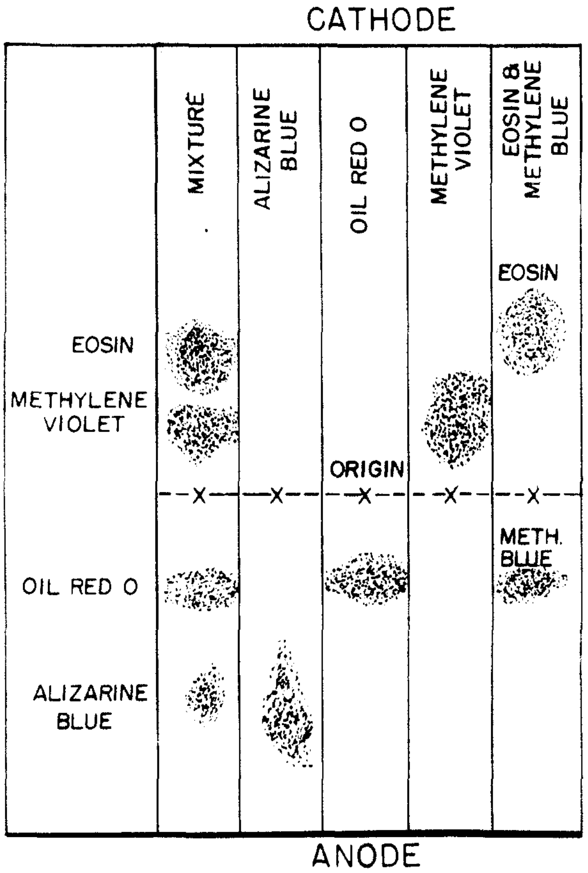

Fig. 2.—Separation of dye mixture in ethyl alcohol; 1000 volts 60 micraomps, 50 min.

was apparent over the short distances traversed. It is perhaps significant that separations were achieved only with ions containing strongly polar groups (the dyes). The migration of the biological substances mentioned may be a passive electroendosmotic effect; however it is possible that these less polar materials could be separated in experiments of longer duration.

The separation of the dye mixtures on the filter paper establishes the feasibility of electrophoretic separations in non-aqueous solvent systems. It is possible that other solvent systems and experimental conditions may provide extension of this technique to a wider range of substances.

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[5] The most highly purified commercially available solvents were employed; however, no effort was made to remove traces of moisture with which the solvents were in equilibrium, since the cell design did not completely exclude atmospheric moisture.

[6] R. J. Williams and H. Kirby, *Science*, **107**, 481 (1948).

The Dissociation Energies of the First and Second Bond in H_2S and Some Comments on a Recent Paper by Franklin and Lumpkin

BY A. H. SEHON[1]

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Franklin and Lumpkin[2] have recently derived a value of 38.4(±5) kcal./mole for ΔH_f(SH) from relevant thermochemical data and their measurements of appearance potentials of carbonium ions

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[1] Post-doctoral fellow, 1951–1952.

[2] J. L. Franklin and H. E. Lumpkin, THIS JOURNAL, **74**, 1023 (1952).

from various mercaptans. Their value agrees fairly well with the value of 32(±4) kcal./mole for $\Delta H_f(\mathrm{SH})$ determined in these laboratories,[3] especially if, as pointed out by them, the heats of formation of radicals obtained by the electron impact method tend to be rather high. Since

$$D(\mathrm{H{-}SH}) = D_1 = \Delta H_f(\mathrm{H}) + \Delta H_f(\mathrm{SH}) - \Delta H_f(\mathrm{H_2S}) \quad (1)$$

and the values for $\Delta H_f(\mathrm{H}) = 52$ kcal./gram atom and for $\Delta H_f(\mathrm{H_2S}) = -4.8$ kcal./mole are well established[4a,b] it is now possible to calculate in terms of the above values for $\Delta H_f(\mathrm{SH})$ the dissociation energy, $D(\mathrm{H{-}SH})$, of the first bond in H_2S (denoted by D_1) at 95(±5) or 89(±4) kcal./mole, respectively.

Furthermore, the dissociation energy $D(\mathrm{S{-}H})$ of the second bond in H_2S (denoted by D_2) can be calculated by the similar expression

$$D(\mathrm{S{-}H}) = D_2 = \Delta H_f(\mathrm{S}) + \Delta H_f(\mathrm{H}) - \Delta H_f(\mathrm{SH}) \quad (2)$$

Unfortunately, it is impossible at present to decide on one particular value for D_2 since in equation (2) $\Delta H_f(\mathrm{S})$ may have one of three values 53.5, 57 or 66.5 kcal./mole[5] depending on the choice of one of the three possible values of 76, 83 or 102.5 kcal./mole for $D(\mathrm{S{-}S})$ in S_2.[6] Hence, D_2 can be 67, 70.5 or 80 kcal./mole on the basis of Franklin and Lumpkin's value for $\Delta H_f(\mathrm{SH})$ or 73.5, 77 or 86.5 kcal./mole on the basis of our value for $\Delta H_f(\mathrm{SH})$.

By adding equations (1) and (2) it follows that the sum of the two S–H dissociation energies in H_2S can vary between 162 and 175 kcal./mole depending on whether $D(\mathrm{S{-}S})$ is taken as 76 or 102.5 kcal./mole. The uncertainty in choosing a particular value for $D(\mathrm{S{-}S})$ is due to the difficulty of interpreting unambiguously the spectrum of S_2. However, Gaydon[6] after analyzing all relevant data is inclined to favor the highest value. From recent interpretations of the S–H spectrum Porter[7] and Ramsay[8] deduce values of 85 and 83 kcal./mole, respectively, for D_2. These, in conjunction with the values given above for D_1 support also the highest value for $D(\mathrm{S{-}S})$.

Franklin and Lumpkin disagree with Porter's value for D_2 and suggest instead a value of 67 kcal./mole. Since the sum of their values for D_1 and D_2, respectively, 95 and 67 kcal./mole, is 162 kcal./mole it appears that they tacitly assumed the lowest value for $D(\mathrm{S{-}S})$. Indeed, an analysis of their results indicates that they used this value throughout their calculations. They argue that if Porter's value of 85 kcal./mole for D_2 is correct then D_1 must be 77 kcal./mole, *i.e.*, D_1 would then be smaller than D_2, which is contrary to what one would expect by comparison with the corresponding bond strengths in H_2O. It seems, therefore, that their arbitrary choice of the lowest value for $D(\mathrm{S{-}S})$ is the only reason for their disagreeing with Porter's value for D_2. Surprisingly, however, in spite of their method of calculation they suggest that on general chemical grounds the highest value for $D(\mathrm{S{-}S})$ appears to be the correct one.

Thus if $D(\mathrm{S{-}S})$ is, indeed, 102.5 kcal./mole then the sum of the two dissociation energies in H_2S is 175 kcal./mole, and since a value of ~90 kcal./mole for D_1 is supported by both electron impact and pyrolytic methods, D_2 will be ~85 kcal./mole, which is in reasonable agreement with Porter's and Ramsay's values obtained spectroscopically. A final settlement of this point can only be reached by an unambiguous determination of $D(\mathrm{S{-}S})$ or $\Delta H_f(\mathrm{S})$.

Note: Franklin and Lumpkin give $D(\mathrm{HS{-}SH}) = 80.4$ kcal./mole, a value, which was presumably obtained by them by using in their calculations $\Delta H_f(\mathrm{H_2S_2})_{\mathrm{liq}} = -3.6$ kcal./mole instead of $\Delta H_f(\mathrm{H_2S_2})_g$, as required. Since the heat of vaporization of H_2S_2 is probably ~8 kcal./mole, it follows that $D(\mathrm{HS{-}SH})$, based on their value for $\Delta H_f(\mathrm{SH})$, should have actually been 72.4 kcal./mole. On the other hand on the basis of our value for $\Delta H_f(\mathrm{SH})$ $D(\mathrm{HS{-}SH})$ is 59.6 kcal./mole, a value which is comparable with $D(\mathrm{HO{-}OH})$ of 54 kcal./mole.[9]

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[3] This value has been calculated by using the data of our determination of $D(\mathrm{CH_3{-}SH})$ by the "toluene-carrier" technique [A. H. Sehon and B. deB. Darwent, A. C. S. Meeting, Buffalo, March, 1952. A full account will be published shortly].

[4] (a) Selected Values of Chemical and Thermodynamic Properties, N. B. S., Washington, 1947; (b) K. K. Kelley, U. S. Dept. of Interior, Bureau of Mines, Bulletin 406 (1937).

[5] Since $[\Delta H_f(\mathrm{S}) = (\Delta H_f(\mathrm{S_2})_g + D(\mathrm{S{-}S})]/2$ where $\Delta H_f(\mathrm{S_2})_g = 30.80$ kcal./mole. [W. H. Evans and D. D. Wagman, Natl., Bur. Standards, Report No. 1037, Washington, 1951.]

[6] A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," Chapman and Hall, Ltd., London, 1947.

[7] G. Porter, *Discussion Faraday Soc.*, **9**, 60 (1950),

[8] D. A. Ramsay, *ibid.*, 80 (1950),

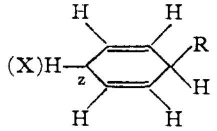
[9] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

Quantum Mechanical Calculations of Orientation in Aromatic Substitution[1]

BY JOHN D. ROBERTS AND ANDREW STREITWIESER, JR.[2]

RECEIVED MARCH 11, 1952

Wheland[3] has shown definitely that the molecular orbital method makes possible a single unified treatment of electrophilic, free-radical and nucleophilic substitution reactions of aromatic molecules. His approach was based on calculations of the energies of activated complexes of type I where z is a unit positive charge, an unpaired electron or a unit negative charge depending on whether the attacking reagent (R) is an electrophilic, radical or nucleophilic species.



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With various substituent groups (X) and reasonable assignments to appropriate parameters, he found that the pattern of aromatic substitution could be well reproduced.

In the present work, the simple molecular orbital

[1] Supported by the research program of the U. S. Atomic Energy Commission under Contract AT(30-1)905.

[2] U. S. Atomic Energy Commission Post-Doctoral Fellow, 1951–1952.

[3] G. W. Wheland, THIS JOURNAL, **64**, 900 (1942).