value of ΔH_f° at 298.16°K. (Table VIII) and the thermodynamic functions of C(graphite),[18] H_2(gas)[18] and S_2(gas)[20] were used in computing values of ΔH_f°, ΔF_f° and $\log_{10} K_f$ at selected temperatures from 0 to 1000°K. The calculated values of these eight thermodynamic properties are recorded in Table XI.

Acknowledgments.—The authors wish to thank Dr. E. J. Rosenbaum, Sun Oil Company, for making spectroscopic data available before publication. We also thank Mr. T. G. Burke, Carbide and Carbon Chemicals Company, for determining the infrared spectra from 25–40 μ and for granting permission to publish the curves in Fig. 1.

BARTLESVILLE, OKLA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Electronic Structure of Conjugated Sulfur Compounds. I. Thiophene and Isothianaphthene

BY JOSEPH DE HEER

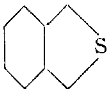
RECEIVED MARCH 11, 1954

The electronic structure of thiophene and isothianaphthene has been calculated by means of a molecular orbital scheme as developed by Longuet-Higgins. Our results suggest a marked difference in homolytic and heterolytic reactivity of certain centers in these molecules. This is in general accordance with experiment. Some experimental data, which only recently have become available, are briefly reviewed. The popular attempts to relate all properties of conjugated sulfur compounds to isosteric polyenes are criticized.

1. General Introduction

It has been emphasized for quite some time that there is often a close similarity in physical and chemical properties between aromatic hydrocarbons and the corresponding compounds in which a —CH=CH— group is replaced by a sulfur atom. Thus, following Victor Meyer who pioneered in this field, many investigators have mentioned such similarities between benzene and thiophene.[1]

Recently, Dann, *et al.*,[2,3] have reported an investigation of the isothianaphthene (benzo[c]-thiophene) ring system (I).



I

In particular they investigated the diene additions of certain compounds containing this ring system. The results suggest not only a detailed discussion of the reactivity of this molecule, but also a reconsideration of the properties of thiophene itself. It becomes obvious that similarities between benzene and thiophene are largely confined to those properties relating to size, shape, molecular weight, etc. The experimental evidence, which will be reviewed in section 6 of this paper, suggests strongly that heterolytic reactivity (relating to nitration, sulfonation, etc.) and homolytic reactivity (*e.g.*, diene additions[4]) should be clearly distinguished.

In this paper we present a theoretical discussion of these reactivities as related to the electronic structure of thiophene and isothianaphthene, on the basis of a molecular orbital theory developed by Longuet-Higgins.[5] A few brief, semi-quantitative, remarks about the ultraviolet spectra of these compounds will be included.

2. Free Valencies, Charge Densities and Self-polarizabilities, as a Measure for the Homolytic and Heterolytic Reactivity in Aromatic Hydrocarbons.—Strictly speaking the reactivity of aromatic hydrocarbons (as of all molecules) should be discussed in terms of their *dynamic* behavior in going into a transition state with a specific reagent. Where such a procedure is too involved, useful indications may be obtained by considering certain *static* properties of these molecules, in particular with reference to their π electron system.

(a) **Free Valencies.**—In this paper free valencies are obtained on the basis of the molecular orbital method, following a procedure originally outlined by Coulson.[6,7] As is well known, these quantities, which indicate the "availability" of electrons at the various positions in a hydrocarbon, are a measure for the homolytic reactivity of these centers.

(b) **Charge Densities and Self-polarizabilities.**—To a first approximation the π electron charge densities at all centers in aromatic and olefinic hydrocarbons are equal to 1. This is equally true for the carbon centers in thiophene, when its electronic structure is described by the Longuet-Higgins theory[5] (see section 3 below). Therefore, in all these molecules, charge densities cannot determine the difference in heterolytic reactivity of the various positions. Here the important quantities are the "self-polarizabilities"[8,9] of the centers concerned. In fact, these polarizabilities determine quantitatively the susceptibility to what most physical organic chemists call, following Ingold, an "electromeric effect."

3. Electronic Structure of Thiophene.—Up till 1939, it was generally assumed that in thiophene

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[1] For a survey, see H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952.

[2] O. Dann, M. Kokorudz and R. Gropper, *Chem. Ber.*, **86**, 1449 (1953); **87**, 140 (1954).

[3] O. Dann and H. Distler, *ibid.*, **87**, 365 (1954).

[4] According to C. K. Ingold ("Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953), diene additions are largely, but not wholly, homolytic.

[5] H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

[6] See, *e.g.*, *Faraday Soc. Discs.*, **2**, 9 (1947).

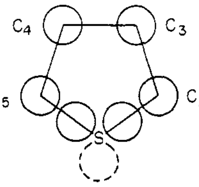
[7] See appendix I for a brief discussion of this procedure and suggested alternatives.

[8] C. A. Coulson and H. C. Longuet-Higgins, *La Revue Sci.*, **85**, 929 (1947).

[9] See appendix II for an explicit definition of self-polarizabilities and a brief summary of the relevant arguments of reference 8.

the S atom participates in conjugation by virtue of its two 3p electrons, in much the same way as the O atom, through its two 2p electrons, is active in furane. In 1939 Pauling and Schomaker,[10] in their description of the π electron system in thiophene, included "resonance hybrids" in which the sulfur atom had expanded its valence shell to ten electrons. This implies that 3d sulfur orbitals participate in the bonding process, which is a reasonable assumption since the energy difference between 3p and 3d is not too high.[11] (Obviously a similar situation for oxygen is very unlikely since it would require excitation from 2p to 3d.) In 1949 Longuet-Higgins[5] showed that we may form three pd_2 hybrid orbitals for sulfur, two of which have the correct symmetry and energy to conjugate with the carbon atoms.

The third hybrid orbital is too high in energy to be occupied in the ground state. The situation is very schematically illustrated in the diagram below (the dotted contour represents the unoccupied hybrid).

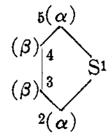


This immediately gives a *qualitative* explanation of the similarity between –S– and —CH=CH— in conjugated systems. *Quantitatively* Longuet-Higgins could show that within the simple L.C.A.O. approximation, all molecular orbital parameters for the π electron sextet in thiophene are exactly like those in benzene, except for two resonance integrals (the ones between the S hybrids, and the C_2 and C_5 carbon $2p_z$ atomic orbitals), which are reduced by 20%. For details of the elaborate analysis, which led to these conclusions, we refer to the original paper by Longuet-Higgins.[5] In that paper, applications were largely confined to resonance energy, dipole moment and bond lengths in thiophene itself. Chemical reactivity was only barely touched upon: The reactivity of the C_2–C_5 system in thiophene should, according to Longuet-Higgins, be intermediate between that of benzene and that of butadiene, being closer to the former. In subsequent paragraphs we shall take up this matter more explicitly. In this connection it is important to realize that (a) since all π electron charge densities in thiophene are 1 (according to the Longuet-Higgins theory all Coulombic integrals are the same!), differences in heterolytic reactivities of C_α and C_β will be determined by differences in self-polarizability of these centers (see section 2 above and appendix II); (b) it should be possible to treat isothianaphthene along the same lines as thiophene. The ten π electrons should be considered in a field consisting of one "ordinary" benzene ring to which is attached, in the proper fashion, a "distorted" benzene ring as described above.[12]

4. Mobile Bond Orders and Free Valencies in Thiophene and Isothianaphthene.—In order to calculate free valencies,[6,7] we first have to know the relevant mobile bond orders, p_{rs}. For thiophene itself, these bond orders were already obtained by Longuet-Higgins from those in benzene by the application of a very simple perturbation method.[5,12,13] Since in the present investigation we are confronted with some fairly small differences in free valencies, we decided to recalculate the bond orders in thiophene by the more accurate[13] direct method, that is from the explicit forms of the occupied molecular orbitals. Similar calculations were carried out for isothianaphthene, this molecule being treated as indicated at the end of the preceding paragraph. Details of the calculations, which follow well known standard procedures, will not be reported.

The results are as follows

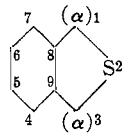
Thiophene



Mobile bond orders

$p_{12} = p_{15} = 0.582$
$p_{23} = p_{45} = 0.727$
$p_{34} = 0.612$
[Compare: Benzene: $p_{rs} = 0.667$
Butadiene: $p_{12} = p_{34} = 0.894$
$p_{23} = 0.447$]

Isothianaphthene



Mobile bond orders

$p_{12} = p_{23} = 0.646$
$p_{18} = p_{39} = 0.608$
$p_{89} = 0.489$
$p_{78} = p_{49} = 0.537$
$p_{67} = p_{45} = 0.736$
$p_{56} = 0.589$

These data *as such* do not interest us in the present investigation. (The theoretical bond orders in thiophene have been compared with experimental bond lengths[10] by Longuet-Higgins.[5]). They lead directly to the important free valencies.[6,7] The results of our calculations for thiophene and isothianaphthene, together with some known values for butadiene, benzene, naphthalene and anthracene are compiled in Table I. For a discussion, see paragraph 6 below.

5. Self-polarizabilities and Conjugating Powers in Thiophene and Isothianaphthene.—Since the explicit expressions for the occupied molecular orbitals are known from the work reported in the previous section, it is a simple matter to calculate the relevant self-polarizabilities.[9,14] Again our results for thiophene and isothianaphthene are tabulated together with a number of known values of polyene systems (Table I). It has been shown by Coulson and the present author[15] that the square roots of the self-polarizabilities act as "conjugating powers" of the residues concerned. Although these quantities are of no concern to us

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[10] L. Pauling and V. Schomaker, THIS JOURNAL, **61**, 1779 (1939).

[11] The participation of 3d orbitals of sulfur may also account for its conjugative properties in sulfones; see H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

[12] The first successful application of the Longuet-Higgins theory to a larger molecule, in fact to the calculation of bond orders and bond lengths in thiophthen (thieno[3,2-b]thiophene), was given by M. G. Evans and the present author; see M. G. Evans and J. de Heer, *Acta Cryst.*, **2**, 363 (1949).

[13] In appendix III the perturbation method is briefly outlined, and the results thereof are compared with those of direct calculations, as performed in the present investigation.

[14] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A191**, 39 (1947); **192**, 16 (1947).

[15] C. A. Coulson and J. de Heer, *J. Chem. Soc.*, **92**, 483 (1952).

TABLE I

Molecule and position	Free valency[a]	Molecule and position	Self-polarizability (in units $1/\beta$[b])	Conjugating power (in units $1/\sqrt{\beta}$[b])
β-Thiophene	0.34	Benzene	0.398	0.631
2-Butadiene	.34	β-Thiophene	.400	.632
Benzene	.34^5	2-Butadiene	.402	.634
β-Naphthalene	.35	β-Naphthalene	.405	.636
5-Isothianaphthene	.35^5	5-Isothianaphthene	.408	.639
2-Anthracene	.35^5	2-Anthracene	.411	.641
		α-Naphthalene	.443	.666
		α-Thiophene	.451	.672
α-Thiophene	.37	4-Isothianaphthene	.452	.673
		1-Anthracene	.454	.674
α-Napthalene	.40			
4-Isothianaphthene	.40^5			
1-Anthracene	.40^5			
		α-Isothianaphthene	.525	.724
		9-Anthracene	.526	.725
α-Isothianaphthene	.42^5			
		1-Butadiene	.626	.791
9-Anthracene	.47			
(1-Butadiene	.79)			

[a] The *absolute* values of these data are *insignificant*. Alternative schemes for calculating free valencies would lead to the *same relative values*, except perhaps for 1-butadiene, the free valency of which is therefore given with some reservation (see Appendix I for a clarification of this point). [b] β is the resonance integral in benzene; it is a *negative* quantity.

within the scope of the present investigation, we have included them in Table I for future reference.

6. Discussion; Comparison with Experiment.—The most important conclusion to be drawn from Table I is that there are a few important differences in the sequence of free valencies as compared with the sequence of self-polarizabilities. Whereas the free valencies of α-thiophene and α-isothianaphthene clearly fall in between those of benzene and α-naphthalene, and of α-naphthalene and 9-anthracene, respectively (in both cases being closer to the one first mentioned), the self-polarizabilities of α-thiophene and α-isothianaphthene are of the same magnitude as those of α-naphthalene and 9-anthracene. No such "anomaly" exists for the β-positions (or centers farther away from the sulfur atom); here both free valencies and self-polarizabilities are comparable with those of the "corresponding hydrocarbon" (–S– replaced by —CH═CH—).

These observations explain some marked differences in homolytic and heterolytic reactivity as suggested by the experimental material reported by Dann, *et al.*[2,3] In heterolytic reactions (nitration, sulfonation) thiophene "acts like one naphthalene ring," the α-position being far more reactive than the β-position. In this connection Dann and Distler also mention the dissociation constants of the α- and β-carbonic acids in which again there is a striking similarity between thiophene and naphthalene. On the other hand, Dann and Distler report that, whereas a diene addition with maleic anhydride can be carried out successfully with 1,2,3,4-tetramethylnaphthalene, no adduct could be isolated with 2,3,4,5-tetramethylthiophene. Making the reasonable assumption that the four methyl groups activate the two diene systems to the same extent, we may conclude that the homolytic reactivity of the α-thiophene centers are markedly less than those of α-naphthalene. This is indeed the result found by our free valency calculations. Theory suggests that in this respect thiophene should be more reactive than benzene. Since so far the only evidence from experiments is that both do not react, we have as yet no experimental check on this aspect of our theoretical results.

Unsubstituted isothianaphthene has not been prepared as yet, and hence data on its heterolytic reactivity are not available. Its homolytic reactivity was established by Dann and Kokorudz[2] on the basis of the maleic anhydride addition of 1,3,4,7-tetramethylisothianaphthene and of 4,5,6,7-dibenzoisothianaphthene, as compared with the same addition of analogous naphthalene and anthracene derivatives. The conclusion was drawn that the homolytic reactivity of the isothianaphthene ring system falls in between that of naphthalene and anthracene. This again is confirmed by our free valency calculations. Our theory predicts a closer resemblance with naphthalene than with anthracene (in complete contradiction to the *heterolytic* reactivity of α-isothianaphthene which should be of exactly the same order as that of 9-anthracene), but unfortunately the semi-quantitative nature of the experimental evidence does not justify a more accurate comparison. In this connection it is to be hoped that quantitative experiments, giving explicit rate constants and (or) equilibrium constants, obtained under strictly comparable conditions, will be carried out in this field.

7. Ultraviolet Spectra.—The close similarity in ultraviolet spectra of compounds with –S– replacing —HC═CH— has been emphasized by many authors.[16] Within the framework of the Longuet-Higgins description of conjugated sulfur compounds such a similarity is not surprising. Price and Morita[16h] find that the unsaturated sulfide has its absorption at somewhat longer wave length than the corresponding polyene. Our calculations on the L.C.A.O. molecular orbitals, which are not reported in detail in this paper, indeed indicate a slight convergence of the energy levels in the sulfur compound as compared with the "corresponding" polyene. However, we do not wish to attach undue importance to this point, since a sound treatment of electronic spectra would require a much more sophisticated theory. We do think it important to emphasize that we ought to distinguish two cases.

(a) Molecules in Which the π Electron Systems in the Sulfur Compound and the "Corresponding" Polyene Have the Same Symmetry.—Here we have the most striking resemblance in spectra; an example is provided by divinyl sulfide and 1,3,5-hexatriene.[16f] The slight shift to longer wave lengths in the former molecule should ultimately arise from the distortion due to the two reduced resonance integrals (see section 3 above). This distortion does *not* change the symmetry of the π electron system in this molecule.

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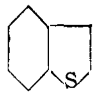
(16) (a) G. Millazzo, *Experientia*, **3**, 370 (1947); (b) A. D. Walsh, *Quart. Revs.*, **2**, 85 (1948); (c) M. R. Padhye and S. R. Desai, *Proc. Phys. Soc.*, **A65**, 298 (1952); (d) M. R. Padhye and J. C. Patel, *Trans. Faraday Soc.*, **49**, 1119 (1953); (e) M. R. Padhye and S. R. Desai, *ibid.*, **49**, 1386 (1953); (f) C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950); (g) C. C. Price and R. G. Gillis, *ibid.*, **75**, 4750 (1953); (h) C. C. Price and H. Morita, *ibid.*, **75**, 4747 (1953).

(b) **Molecules in Which the π Electron Systems in the Sulfur Compound and the "Corresponding" Polyene Have Different Symmetry.**—Here we have an *additional* effect: The symmetry may exclude certain transitions in the polyene, which are allowed in the sulfur compound. Thus Padhye and Patel[16d] found bands in the spectrum of thianaphthene (II), which are electronically forbidden in naphthalene. Obviously this additional "symmetry effect" should be the more important as the loss in symmetry in going from the polyene to the sulfur compound is more marked. Thus this effect should have considerable consequences in going from the sixfold symmetry of benzene to the twofold symmetry of thiophene. This explains the observation of Dann and Distler[3] that the thiophene spectrum does not show much resemblance with that of benzene.



II

In our opinion the observation of Dann and Kokorudz,[2] that the ultraviolet spectrum of isothianaphthene is intermediate between that of naphthalene and anthracene (and closer to the latter) is without any sound foundation for the following reasons: (i) The "analogy" only applies to part of the spectral range measured.[2] (ii) Not the spectrum of isothianaphthene, but that of 1,3,4,7-tetramethylisothianaphthene was used for this comparison with *unsubstituted* naphthalene and anthracene. The effect due to the four methyl groups, should be taken into account. (iii) Theoretically the comparison makes no sense since isothianaphthene and anthracene have a different number of π electrons (10 and 14, respectively) in addition to a different symmetry. Here a further investigation, both experimentally and theoretically, seems desirable.

Acknowledgment.—The author wishes to thank Dr. Otto Dann of Erlangen University, for drawing his attention to the problems discussed in this paper and for enabling him to read the manuscripts concerned prior to publication. He also wishes to thank the Council on Research and Creative Work at the University of Colorado for a grant in aid of this investigation.

Appendix I

Free Valencies.—In computing the free valencies (f.v.) on Table I we have used the formula[6]

$$(\text{f.v.})_r = N_{\max} - C_r - \sum_s p_{rs} \qquad (1)$$

Here C_r is the contribution from the basic σ bonds, to which center r is connected, it is equal to 3 in all our applications. $N_{\max}$ is a constant, which usually has been taken to be equal to 4.680. Hence (1) reduces to the simple formula

$$(\text{f.v.})_r = 1.680 - \sum_s p_{rs} \qquad (2)$$

Two points must be mentioned in connection with eq. 2: (a) Moffit[17] has pointed out that 4.730 should be used instead of 4.680 if one wishes to include free radicals. (b) Burkitt, Coulson and Longuet-Higgins[18] have suggested an alternative scheme, using different values for $N_{\max}$ in the case of primary, secondary and tertiary carbon atoms. Greenwood,[19] however, has shown that little can be gained from this alternative scheme, and a great deal is lost both in simplicity of formulation and in the physical significance of the quantities so derived.

In our paper free radicals do not enter the discussion and we are exclusively interested in secondary carbon atoms. Thus, modification of (2) on the basis of (a) and (b) above would merely change all data of Table I by a constant amount, which would be of no significance. (Only the comparison value for 1-butadiene must be taken with some reservation in this respect.)

Appendix II

Self-polarizabilities and their Role in Determining Heterolytic Reactivities.—If we let a charged reactant approach center r in a conjugated system the variation of the total energy of the π electrons in that system, E, is largely a result of the variation in α_r, the Coulomb integral of center r. Following Coulson and Longuet-Higgins,[8] we thus can develop dE in a Taylor series

$$\begin{aligned} dE &= \frac{\partial E}{\partial \alpha_r} \times d\alpha_r + (1/2)\frac{\partial^2 E}{\partial \alpha_r^2} \times (d\alpha_r)^2 \\ &= q_r \times d\alpha_r + (1/2)\pi_{rr} \times (d\alpha_r)^2 \end{aligned}$$

Here

q_r = the π electron charge density on center r

π_{rr} = the self-polarizability of center r

As mentioned in this paper (sections 2b and 3) all q_r for the molecules under consideration are equal to 1. Hence differences in dE, which in turn should reflect differences in activation energy for heterolytic reactions, are determined by π_{rr}. Now all π_{rr} are negative (see footnote to Table II) and of course $(d\alpha_r)^2$ is positive, no matter whether $d\alpha_r$ is positive (nucleophilic reagent) or negative (electrophilic reagent). Thus the larger the absolute value of π_{rr} (the larger the numerical value of π_{rr} in Table I), the smaller dE, the greater the heterolytic reactivity. Here we have a quantitative description of the "electromeric effect,"[4] which is always such as to facilitate reaction.

The π_{rr} may be calculated numerically if the explicit forms of the occupied molecular orbitals are known. We have[14]

$$\pi_{rr} = 4\sum_j \sum_k \frac{c^2_{rj}\, c^2_{rk}}{\epsilon_j + \epsilon_k} \qquad (3)$$

where c_{rj} is the coefficient of the atomic orbital ϕ_r in the jth occupied molecular orbital, energy ϵ_j. Equation 3 has been used in our computations of the self-polarizabilities of the various centers in thiophene and isothianaphthene (see Table I).

Appendix III

Accuracy of the Perturbation Method.—Since the π-electron system in thiophene is obtained

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[17] Quoted by C. A. Coulson, *J. chim. phys.*, **45**, 243 (1948).

[18] F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

[19] H. H. Greenwood, *ibid.*, **48**, 677 (1952).

from that in benzene by changing two resonance integrals (β_{12} and β_{56} for example) by a relatively small amount, all quantities in the former molecule should be obtained from those in the latter by some simple perturbation calculation. Thus for the mobile bond orders we have *e.g.*[5]

$$(p_{34})_{\text{thiophene}} = (p_{34})_{\text{benzene}} + \left(\frac{\partial p_{34}}{\partial \beta_{12}}\right)_{\text{benzene}} \times \delta\beta_{12} + \left(\frac{\partial p_{34}}{\partial \beta_{56}}\right)_{\text{benzene}} \times \delta\beta_{56} \quad (4)$$

(numbering of thiophene: See section 4 of this paper; 1 and 6 refer to the conjugating sulfur hybrids.) The quantities $(\partial p_{rs}/\partial \beta_{tu})$ are written $\pi_{rs,tu}$ and called "*mutual bond polarizabilities.*" They may readily be calculated[14,20] for benzene and naphthalene. For benzene we find, for example[20]

$$\pi_{34,12} = \pi_{34,56} = 7/(54\beta)$$

In benzene all bond orders p_{rs} are 0.667. With $\delta\beta_{12} = \delta\beta_{56} = -(1/5)\beta$, (4) finally yields

$$(p_{34})_{\text{thiophene}} = 0.667 - \frac{2 \times 7}{5 \times 54} = 0.615$$

in good agreement with the direct calculation, which yielded 0.612 (see section 4 above). In Table II we have collected all mobile bond orders in thiophene and isothianaphthene, calculated (i) directly, (ii) by the perturbation method.

TABLE II

MOBILE BOND ORDERS IN THIOPHENE AND ISOTHIANAPHTHENE, CALCULATED DIRECTLY AND BY PERTURBATION METHOD

Numbering: See section 4 of this paper.

	Thiophene			Isothianaphthene	
	Direct	Perturbation		Direct	Perturbation
$p_{12} = p_{15}$	0.582	0.593	$p_{12} = p_{23}$	0.646	0.658
$p_{23} = p_{45}$	.727	.726	$p_{18} = p_{39}$	.608	.608
p_{34}	.612	.615	p_{89}	.489	.491
			$p_{78} = p_{49}$	.537	.538
			$p_{67} = p_{45}$	.736	.735
			p_{56}	.589	.590

In general the perturbation method yields satisfactory results, except for the C–S bonds which come out 0.010 to 0.012 too high. Unpublished calculations by L. R. Blue and the present author indicate a similar discrepancy in some other conjugated sulphur compounds. Thus the perturbation method would give free valencies for α-carbon atoms which are about 0.01 too low. Since we are interested in small differences in free valencies, such deviations are undesirable.

Our conclusion is that direct calculations should be given preference if not too much labor is involved. The perturbation method however leads to generally good results, in particular if an empirical correction of −0.01 is applied to the mobile bond orders of all C–S bonds.

BOULDER, COLORADO

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[20] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (*London*), **A193**, 447 (1948).

[CONTRIBUTION NO. 3376 FROM DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH LABORATORIES]

The Thermal Decomposition of Mercaptans

BY A. H. SEHON[1a] AND B. deB. DARWENT[1b]

RECEIVED FEBRUARY 1, 1954

The thermal decompositions of benzyl, methyl and ethyl mercaptans have been investigated in a flow system in the presence of a large excess of toluene as a carrier gas and a free radical trap. Benzyl mercaptan decomposes by a homogeneous, first-order free radical process with an activation energy of 53(±2) kcal. mole^{-1}, which has been identified with the dissociation energy of the C–S bond. Methyl mercaptan also decomposes by a free radical mechanism but the process is more complicated. The activation energy, identified with the C–S bond dissociation energy, was calculated to be 67 kcal. mole^{-1} on the assumption of a constant frequency factor. Ethyl mercaptan decomposes principally by intermolecular rearrangement to C_2H_4 and H_2S and also by a split of the C–S bond to yield ethyl and hydrosulfide radicals. The molecular process appears to be somewhat heterogeneous with an activation energy that decreases from about 55 kcal. mole^{-1} to about 48 kcal. mole^{-1} with decreasing temperature. The activation energy for the free radical reaction, which is identified with the C–S bond dissociation energy, was calculated to be 63.5 kcal. mole^{-1} on the assumption of a constant frequency factor. From the above values of D(CH_3–SH) and D(C_2H_5–SH) together with relevant thermochemical data the heat of formation of the SH radical was estimated to be 32 and 31 kcal. mole^{-1}, in reasonable agreement with the value of 38.4 (±5.0) kcal. mole^{-1} derived by Franklin and Lumpkin from the appearance potentials of carbonium ions from various mercaptans.

Introduction

Although the properties of bonds between sulfur and carbon are of considerable theoretical and practical importance there is very little quantitative information available about the dissociation energies of such bonds or about the mechanisms and kinetics of the thermal decomposition of organic sulfur compounds. Thus there is disagreement about such fundamental quantities as the heat of formation of sulfur atoms and the dissociation energies of the bonds in H_2S.

Porter[2a] and Herzberg and Ramsay[2b] have estimated spectroscopically the S–H bond dissociation energy in the hydrosulfide radical to be about 85 kcal. mole^{-1}. Franklin and Lumpkin,[3] from the appearance potentials of carbonium ions from various mercaptans and relevant thermochemical data, have derived a value of 38.5 (±5) kcal. mole^{-1} for the heat of formation of the hydrosulfide radical. This may be shown[4] to lead to

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[1] (a) N.R.C. Post-Doctoral Fellow 1951–1952; Department of Experimental Medicine, McGill University, Montreal, P. Que.; (b) Olin Industries, Inc., New Haven, Connecticut.

[2] (a) G. Porter, *Disc. Faraday Soc.*, No. 9, 60 (1950); (b) G. Herzberg and D. A. Ramsay, *ibid.*, No. 9, 80 (1950).

[3] J. L. Franklin and H. E. Lumpkin, THIS JOURNAL, **73**, 1023 (1952).

[4] (a) A. H. Sehon, *ibid.*, **74**, 4722 (1952); (b) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).