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Heats of Formation of Organic Molecules by Ab Initio Methods: Thiaalkanes

Norman L. Allinger* and Linrong Yang

Department of Chemistry, School of Chemical Sciences, University of Georgia, Athens, GA 30602, U.S.A.

Ioan Motoc†

Bristol-Myers-Squibb Corporation, Pharmaceutical Research Institute, Princeton, NJ 08543-4000, U.S.A.

Charles Bender and Jan K. Labanowski

Ohio Supercomputer Center, Ohio State University, 1224 Kinnear Road, Columbus, OH 43212-1163, U.S.A.

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ABSTRACT

The bond energy scheme for calculating heats of formation of organic molecules from ab initio data (6-31G) has been extended to include 24 compounds containing sulfur in the sulfide oxidation state. The rms deviation from the experimental values for these compounds is 0.54 kcal/mol, which is approximately experimental error.*

INTRODUCTION

The determination of heats of formation of compounds by calorimetric methods is difficult and extremely time consuming. It also requires a great deal of skill, patience, and expense. With the increasing development of both hardware and calculational methods for carrying out ab initio calculations, it becomes increasingly important to be able to use these calculations to replace highly demanding experimental methods whenever feasible. In earlier work we have shown, following the work of Wiberg [1] and of Ibrahim and Schleyer [2], that coupling a bond energy scheme similar to that used in molecular mechanics to ab initio data, one can calculate heats of formation to within approximately experimental accuracy for several groups of compounds, including alkanes [3], amines [3], alcohols [4], and ethers [4]. Yala [5] has extended the Wiberg/Schleyer scheme, and his method requires relatively little experimental data. It gives heats of formation that are of less than experimental accuracy, however (rms 1.80 kcal/mol for 62 compounds).

There are some problems using our method with compounds belonging to the acetal class, but it is not clear at present whether these problems stem from calculational difficulties, or whether they are in fact experimental [4]. All of the other compounds mentioned have been dealt with very well by our version of the ab initio methods, using approximate Hartree–Fock calculations with a 6-31G* basis. It is accordingly of interest to extend these calculations in various ways, and in the present work we will discuss the extension to dialkyl sulfides (including mercaptans or thiols), where we have molecules containing a second row atom, which in turn contains lone pairs of electrons.

The general procedures have been described previously [3,4]. The bond energy units for the hydrocarbon portion of the molecule have been

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Dedicated to Prof. Ernest L. Eliel on the occasion of his seventieth birthday.

*To whom correspondence should be addressed.

†Deceased

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previously determined [3], and it is only necessary to find bond energy increments for C-S and S-H bonds, and for methyl, secondary, and tertiary carbons attached to sulfur. We therefore want to establish values for these five parameters using available experimental data, and to fit the data as best as we can using least squares methods. The results are given in Table 1. The bond energy parameters have large values because they correspond to forming those bonds and the atoms themselves from nuclei and electrons. The substitution increments, on the other hand, are small because the difference in stability due to whether the sulfur is attached to a methyl, secondary, or tertiary carbon is small. The numerical values for these substitution increments are qualitatively as previously found for other heteroatom substitutions. If the heteroatom is substituted on a methyl, primary, secondary, or tertiary carbon, there is an increasingly large stabilization (the primary case is our zero of reference). At least part of these increments are thought to result from electron correlation, which we do not include in the present (Hartree-Fock) calculations.

Also, given in Table 1 is the list of the compounds fit, the experimental values for their heats of formation [6,7], and the calculated values, together with the differences between calculation and experiment. The rms deviation is 0.54 kcal/mol over the 24 compounds utilized. Two of the compounds studied were given a weight of zero in the least squares fitting. One because it is obviously an outlier in the statistical treatment. For 2-methyl-1-propanethiol, the calculated value is about 2 kcal/mol greater than the experimental value. When we examine the molecular mechanics heat of formation treatment previously published for this class of compounds [8], we find that in that work the calculated value for H_f was 0.93 kcal/mol more positive than the experimental value. The discrepancy is less in the molecular mechanics work than in the ab initio work, partly because the value was included in the molecular mechanics least squares parameter optimization, and hence deformed the fitting somewhat to minimize the error, while the value was not included here in the ab initio work. But clearly the error is sufficiently large, compared with the rest of the errors in Table 1 (and it is in the same direction in both the molecular mechanics and ab initio results) as to indicate that most of the error is in fact in the experiment, and not in the calculations.

No experimental value is available for isopropyl *t*-butyl sulfide, and the calculated value for that compound is offered as a prediction. The value calculated by MM3 [8] for this compound is -40.91 kcal/mol, which is 0.77 kcal/mol more negative than the ab initio value. The agreement seems adequate.

METHODS

The ab initio Hartree–Fock calculations for all molecules listed in Table 1 were performed with the CADPAC4 [9] and HONDO8 [10] programs using the 6-31G* standard basis set [11]. The starting geometries for these molecules were taken from molecular mechanics calculations using the MM3 program [12]; however, the special r_e parameter set was used. This set was designed to provide bond lengths closer to typical 6-31G* results (i.e., to fit r_e rather than r_g bond lengths [13]). Geometry optimization in the ab initio runs was terminated when the largest component of the gradient was less than 5×10^{-4} Hartree/Bohr.

The calculations were carried out in order to establish values for the five unknown parameters that are unique to sulfides. Other values were carried over from earlier calculations on hydrocarbons [3]. The five values required are two bond energies (C-S and S-H) and three substitution increments (S-SE, S-TE, and S-ME), where these latter represent bonds from the sulfur to secondary carbons, tertiary carbons, and methyl groups, respectively. (Primary carbons are taken as a zero of reference.) The necessary input information is given in Table 1, including the Hartree-Fock energies calculated in the present work, the value of SUMH (which is the heat of formation contributions from the hydrocarbon part of the molecule), and the other quantities, which have the usual definitions [3,4,13]. Also in Table 1 are given the number of times each of these units occurs for each molecule studied.

In Table 2 the results are provided. From the data provided in Table 1, the five unknown parameters are evaluated by least squares methods, and the values for the parameters are as shown. The discrepancy between the calculated heat of formation and the experimental value is given for each compound in Table 2. The standard deviation of the calculation from the experiment is 0.54 kcal/mol. This is approximately the same as the average experimental error.

CONCLUSIONS

The accuracy of the calculated heats of formation of the sulfides herein, together with similar earlier calculations on a variety of compounds [3,4], shows that, at least for many routine cases, it is not necessary to measure experimental heats of combustion. The heats of formation for ordinary monofunctional (unconjugated) compounds (so far, only for the classes indicated) can be determined with approximately experimental accuracy by Hartree-Fock calculations at the 6-31G* level.

TABLE 1. Heat of Formation Input Data (kcal/mol)

Eq	*Wt*	H_f°	*SumH*	*E(6-31G*)*	*Pop*	*Tors*	*T/R*
1	1	-5.4718	18901.637	-274656.869	0.000	-0.420	2.400
2	10	-11.0691	43391.932	-299151.890	0.062	0.000	2.400
3	8	-16.2271	67880.710	-323646.390	0.282	0.420	2.400
4	0	-23.2803	92368.571	-348139.573	0.251	0.420	2.400
5	9	-18.2100	67882.228	-323646.591	0.131	0.000	2.400
6	5	-11.4707	116143.329	-371902.107	0.000	0.420	2.400
7	8	-22.9665	140632.106	-396402.154	0.200	0.000	2.400
8	7	-26.1981	92372.524	-348140.909	0.000	0.000	2.400
9	5	-30.3773	116861.295	-372633.182	0.169	0.420	2.400
10	10	-8.9607	37803.273	-299151.325	0.000	0.000	2.400
11	6	-14.2380	62293.569	-323645.888	0.100	0.420	2.400
12	7	-19.6721	86782.346	-348140.219	0.389	0.840	2.400
13	7	-24.4286	111271.117	-372634.518	0.878	1.261	2.400
14	6	-19.9796	86783.865	-348140.527	0.220	0.840	2.400
15	6	-25.0247	111272.636	-372634.726	0.552	1.261	2.400
16	3	14.4827	61578.641	-322899.741	0.000	0.420	2.400
17	7	-8.1512	86067.417	-347411.591	0.000	0.420	2.400
18	6	-15.1792	110556.188	-371907.585	0.000	0.000	2.400
19	3	-35.3722	135764.457	-397127.594	0.000	0.840	2.400
20	7	-21.6299	86783.865	-348139.974	0.207	0.420	2.400
21	3	-28.0116	111274.161	-372634.556	0.138	0.840	2.400
22	5	-15.3424	110557.713	-371906.832	0.000	0.420	2.400
23	4	-33.9352	135764.457	-397128.397	0.188	0.840	2.400
24	7	-28.9905	111274.161	-372633.188	0.000	0.420	2.400
25	0	0.0000	160254.753	-421620.318	0.000	0.840	2.400
26	7	-45.1486	184745.042	-446110.106	0.000	0.840	2.400

	Compound	*C–S*	*S–H*	*S–SE*	*S–TE*	*S–ME*
1	Methanethiol	1	1	0	0	1
2	Ethanethiol	1	1	0	0	0
3	1-Propanethiol	1	1	0	0	0
4	2-Me-1Propanethiol	1	1	0	0	0
5	2-Propanethiol	1	1	1	0	0
6	Cyclopentanethiol	1	1	1	0	0
7	Cyclohexanethiol	1	1	1	0	0
8	2-Me-2-Propanethiol	1	1	0	1	0
9	2-Me-2-Butanethiol	1	1	0	1	0
10	2-Thiapropane	2	0	0	0	2
11	2-Thiabutane	2	0	0	0	1
12	2-Thiapentane	2	0	0	0	1
13	2-Thiahexane	2	0	0	0	1
14	3-Thiapentane	2	0	0	0	0
15	3-Thiahexane	2	0	0	0	0
16	Thiacyclobutane	2	0	0	0	0
17	Thiacyclopentane	2	0	0	0	0
18	Thiacyclohexane	2	0	0	0	0
19	2, 2-DiMe-3-Thiapentane	2	0	0	1	0
20	3-Me-2-Thiabutane	2	0	1	0	1
21	2-Me-3-Thiapentane	2	0	1	0	0
22	2-Me-1-Thiacyclopentane	2	0	1	0	0
23	2, 4-DiMe-3-Thiapentane	2	0	2	0	0
24	3, 3-DiMe-2-Thiabutane	2	0	0	1	1
25	Isopropyl *t*-Butyl Sulfide	2	0	1	1	0
26	Di-*t*-Butyl sulfide	2	0	0	2	0

TABLE 2. Heats of Formation–Output Data (kcal/mol)

Eq	*Wt*	H_f° *Calc*	H_f° *Exp*	*Difference (Calc-Exp)*	*Compound*
1	1	-4.668	-5.471	0.80	Methanethiol
2	10	-10.698	-11.069	0.37	Ethanethiol
3	8	-15.781	-16.227	0.44	1-Propanethiol
4	0	-21.134	-23.280	2.14	2-Me-1-Propanethiol
5	9	-17.940	-18.210	0.26	2-Propanethiol
6	5	-12.066	-11.470	-0.59	Cyclopentanethiol
7	8	-23.556	-22.966	-0.58	Cyclohexanethiol
8	7	-27.114	-26.198	-0.91	2-Me-2-Propanethiol
9	5	-30.025	-30.377	0.35	2-Me-2-Butanethiol
10	10	-9.067	-8.960	-0.10	2-Thiapropane
11	6	-14.601	-14.237	-0.36	2-Thiabutane
12	7	-19.446	-19.672	0.22	2-Thiapentane
13	7	-24.064	-24.428	0.36	2-Thiahexane
14	6	-20.186	-19.979	-0.20	3-Thiapentane
15	6	-24.861	-25.024	0.16	3-Thiahexane
16	3	14.733	14.482	0.25	Thiacyclobutane
17	7	-8.339	-8.151	-0.18	Thiacyclopentane
18	6	-15.982	-15.179	-0.80	Thiacyclohexane
19	3	-34.807	-35.372	0.56	2, 2-DiMe-3-Thiapentane
20	7	-21.190	-21.629	0.43	3-Me-2-Thiabutane
21	3	-26.907	-28.011	1.10	2-Me-3-Thiapentane
22	5	-16.189	-15.342	-0.84	2-Me-1-Thiacyclopentane
23	4	-33.307	-33.935	0.62	2, 4-DiMe-3-Thiapentane
24	7	-29.335	-28.990	-0.34	3, 3-DiMe-2-Thiabutane
25	0	-40.141	–	–	Isopropyl *t*-Butyl Sulfide
26	7	-44.659	-45.148	0.48	Di-*t*-Butyl sulfide

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[a] Best Values: (C–S) = 130670.677; (S–H) = 125084.283; (S–SE) = -2.904; (S–TE) = -7.926; (S–ME) = 1.785.
[b] The Standard Deviation = 0.542.
[c] Based on 24 equations. Optimization and analysis ignores all equations whose weight is zero.

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[12] The MM3 program is available to all users from the Technical Utilization Corporation, Incorporated, 235 Glen Village Court, Powell, Ohio 43065, to commercial users only from Tripos Associates, 1699 South Hanley Road, St. Louis, MO 63144, and to academic users only from the Quantum Chemistry Program Exchange, University of Indiana, Creative Arts Building 181, 840 State Highway 46 Bypass, Bloomington, IN 47405. The current version is available to run on most types of computers, and interested parties should contact one of the distributors directly.
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