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**NON-LOCAL DENSITY FUNCTIONAL CALCULATION OF
GAS PHASE HEATS OF FORMATION**

Danush Habibollahzadeh[‡], M. Edward Grace, Monica C. Concha,

Jane S. Murray and Peter Politzer*

Department of Chemistry
University of New Orleans
New Orleans, Louisiana 70148

[‡]Present address: State University of New York at Buffalo, Department of Chemistry, Buffalo, New York, 14214

*Author to whom correspondence should be addressed.

Abstract

A general procedure is presented for computing the gas phase heats of formation of a wide variety of organic compounds. ΔE for the formation of the molecule from its elements at 0°K is obtained from density functional calculations (Gaussian 92/DFT) for optimized geometries. This result is converted to ΔH at 298°K by assuming ideal behavior and adding the translational, rotational and vibrational energies. Additive correction terms corresponding to the various coordination states of the carbons, nitrogens and oxygens were developed using a data base of 54 compounds. The experimental ΔH_f° values of these compounds are then reproduced with an average absolute error of 3 kcal/mole and a standard deviation of 4 kcal/mole. For a group of ten test cases that were not part of the data base, the average absolute error is 3.5 kcal/mole and the standard deviation is 4.1 kcal/mole.

Keywords: heats of formation, non-local density functional calculations, organic molecules

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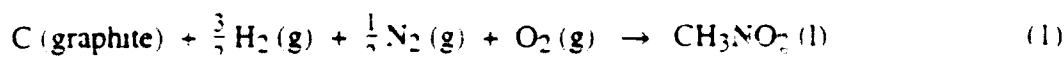
Introduction

In evaluating the potential usefulness of a proposed but not yet synthesized compound, it may be of considerable importance to have a reliable estimate of its heat of formation, ΔH_f , since this can be a key to predicting the compound's thermochemical behavior. A variety of schemes for obtaining heats of formation theoretically have indeed been introduced, based on such concepts as isodesmic and homodesmic reactions, atom equivalents, group equivalents, etc.¹⁻¹²

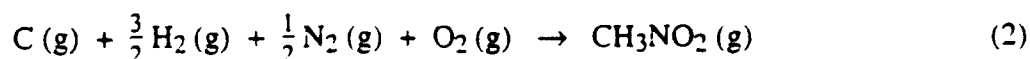
A very direct approach, which we use in this work, is to simply compute ΔH for the formation of the compound from its elements. For this purpose, we wish to exploit the advantages of non-local density functional theory, which permits energies to be calculated for large systems at a level of accuracy comparable to correlated *ab initio* methods.¹³⁻²⁴ Our objective is a general procedure that can be applied to a broad range of organic compounds, and is not limited to any specific classes.

Procedure and Results

The standard heat of formation of a compound, ΔH_f° , is defined as ΔH for the reaction in which it is formed from its elements in their most stable forms, when they and the compound are all at pressures of one bar. Thus, ΔH_f° for liquid nitromethane at 25°C refers to the reaction,



In our computational approach, however, we would calculate ΔE for eq. (2), convert it to ΔH , and then combine the latter with the experimental enthalpy of formation of gaseous carbon and the enthalpy of condensation of gaseous nitromethane.



We compute the optimized geometries and corresponding energies and vibration frequencies for the reactants and product in each formation reaction with the density functional option of Gaussian 92/DFT,²⁵ using the Becke exchange²⁶ and the Perdew-Wang correlation²⁷ functionals and a 6-31G(d,p) basis set. From these energies is determined ΔE .

This ΔE corresponds to 0°K and fixed nuclei. It is converted to ΔE at T°K by adding the translational, rotational and vibrational energies, assuming ideal behavior:⁵

$$\Delta E_{\text{trans}} = \frac{3}{2} RT \quad (3)$$

$$\Delta E_{\text{rot}} = \frac{3}{2} RT \text{ (non-linear molecule)} \quad (4a)$$

$$\Delta E_{\text{rot}} = RT \text{ (linear molecule)} \quad (4b)$$

$$\Delta E_{\text{vib}} = \frac{1}{2} h \sum_i \nu_i + N h \sum_i \nu_i \left[\exp\left(\frac{h\nu_i}{kT}\right) - 1 \right]^{-1} \quad (5)$$

where N is Avogadro's number and the other constants have their usual meanings. ν_i is the vibration frequency of the i^{th} normal mode. Then,

$$\Delta H(T) = \Delta E(T) + (1-n_r)RT \quad (6)$$

where n_r is the total number of moles of gaseous reactants in the formation reaction.

When this approach was used to compute the gas phase heats of formation at 25°C for a group of 54 molecules (primarily organic), the results designated in Table I as "uncorrected" were obtained. While some of these compare well with the experimental values, others are very poor. The average absolute error is 22 kcal/mole.

In order to improve the overall accuracy of this method, we introduced a set of additive correction terms, χ_j . After experimenting with various options, we settled upon having a χ_j for each coordination state of carbon, nitrogen and oxygen. Their values were determined by requiring that the calculated heats of formation reproduce as well as possible the experimental ones in our data base. Thus we minimized the quantity Z ,

$$Z = \frac{1}{m} \sum_{i=1}^m c_i^2 \quad (7)$$

where

$$c_i = \sum_{j=1}^n k_{ij} \chi_j - \Delta_i \quad (8)$$

In eq. (8), the summation is over the n correction terms, each of which is applied k_{ij} times and only on the right side of the formation reaction for molecule i . Δ_i is the error in its calculated

$$\Delta_i = \Delta H_{f,i}^{\circ}(\text{calc}) - \Delta H_{f,i}^{\circ}(\text{exp}) \quad (9)$$

gaseous heat of formation, and m is the number of molecules in the data base, 54. The minimization of Z was carried out by means of a multidimensional pattern search in which all χ_i are varied simultaneously through small steps, the lengths of which are adjusted individually so as to provide the steepest descent of Z .^{28,29}

The resulting correction terms χ_i are listed in Table II. When these are appropriately added to the calculated uncorrected ΔH_f values in Table I, the "corrected" ΔH_f° (calc) are obtained. These reproduce the experimental values quite well; the average absolute error and standard deviation are 3 and 4 kcal/mole, respectively.

In order to test our procedure, we computed the gas phase heats of formation for ten compounds that were not part of the data base used to determine the correction terms, but for which experimental values are known. The results are in Table III. The average absolute error is 3.5 kcal/mole and the standard deviation is 4.1 kcal/mole; these are very similar to what was obtained for the compounds in the data base.

Conclusion

We conclude that the computational approach that has been presented is an effective means for obtaining reliable estimates of the gas phase heats of formation of a wide variety of organic compounds. It is anticipated that the scope and accuracy can be increased by expanding the data base used to obtain the correction terms.

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Table I. Gas phase heats of formation.

Molecule	Heats of formation, kcal/mole.				
	Expt. ^a	Calc., uncorrected	Error	Calc., corrected	Error
chlorodifluoromethane	-115.3	-116.14	-0.8	-110.46	4.8
formic acid	-90.51	-85.91	4.60	-84.40	6.11
1-fluoropropane	-68.33	-82.31	-13.98	-65.27	3.06
urea	-58.75	-61.37	-2.62	-50.56	8.19
water	-57.79 ^b	-42.18	15.61	-47.31	10.48
ethanol	-56.21	-58.77	-2.56	-52.54	3.67
acetone	-51.94	-64.96	-13.02	-46.95	4.99
methanol	-48.16	-44.46	3.70	-43.92	4.24
dimethyl ether	-44.00	-50.41	-6.41	-44.19	-0.19
neopentane	-40.18	-65.36	-25.18	-36.96	3.22
n-butane	-30.02	-53.17	-23.15	-30.45	-0.43
methyl nitrate	-29.21	-43.05	-13.84	-39.21	-10.00
chloroethane	-26.79	-39.57	-12.78	-28.21	-1.42
formaldehyde	-25.96	-25.75	0.21	-19.10	6.86
propane	-25.02	-42.35	-17.33	-25.31	-0.29
nitroethane	-24.45	-42.73	-18.28	-20.11	4.34
ethane	-20.0	-31.63	-11.6	-20.27	-0.3
methane	-17.8	-22.56	-4.8	-16.88	0.9
nitromethane	-17.8	-28.13	-10.3	-11.19	6.6
methyl nitrite	-15.9	-27.80	-11.9	-19.38	-3.5
ammonia	-11.0 ^b	-7.56	3.4	-5.48	5.5
methylamine	-5.50	-11.17	-5.67	-3.42	2.08
isobutene	-4.04	-26.09	-22.05	-2.64	1.40
oxazole	-3.70	-24.26	-20.56	-3.99	-0.29
dimethylnitramine	-1.1	-27.36	-26.3	-2.67	-1.6
propene	4.78	-11.41	-16.19	6.37	1.59
nitroethylene	9. ^c	-9.14	-18.	14.21	5.
4,5-dihydro-3-nitroisoxazole	9.32	-18.84	-28.16	11.96	2.64
1,3,5-triazine-2,4,6-triamine	12.4	-28.24	-40.6	17.95	5.6
chlorobenzene	12.4	-26.88	-39.3	9.39	-3.0
ethylene	12.5	3.53	-9.0	15.63	3.1
cyclopropane	12.7	-4.87	-17.6	12.17	-0.5
1,3-dinitrobenzene	12.9	-41.71	-54.6	17.09	4.2
1,4-dinitropiperazine	13.9	-37.30	-51.2	12.10	-1.8
4-nitroaniline	14.1	-36.71	-50.8	12.91	-1.2
acetonitrile	15.4	5.45	-10.0	15.37	0.0
nitrobenzene	16.1	-31.25	-47.4	16.29	0.2
isoxazole	18.8	-4.78	-23.6	15.49	-3.3
benzene	19.7	-17.32	-37.0	18.95	-0.8
aniline	20.8	-19.71	-40.5	18.64	-2.2
methylhydrazine	22.6 ^b	11.11	-11.5	20.95	-1.7
dimethylfuroxan	24.45	-19.83	-44.28	16.40	-8.05
dimethylfuran	25.65	-13.11	-38.76	19.75	-5.90
pyrrole	25.88	-1.99	-27.87	24.27	-1.61

(continued)

Table I. Gas phase heats of formation (continued).

Molecule	Heats of formation, kcal/mole.				
	Expt. ^a	Calc., uncorrected	Error	Calc., corrected	Error
1,3-butadiene	26.29	4.26	-22.03	28.44	2.15
indole	37.40	-17.17	-54.57	33.28	-4.12
propyne	44.19	31.32	-12.87	42.64	-1.55
allene	45.53	26.95	-18.58	45.08	-0.45
1,3,5-trinitro-1,3,5-triazacyclohexane	45.8 ^d	-16.96	-62.8	40.09	-5.7
pyrimidine	46.82	8.39	-38.43	47.11	0.29
pyrazine	46.87	12.00	-34.87	50.73	3.86
acetylene	54.54	50.44	-4.10	56.09	1.55
pyridazine	66.52	28.78	-37.74	67.51	0.99
tetrazole	79.95	49.52	-30.43	79.46	-0.49

^aUnless otherwise indicated, experimental values are from J. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman and Hall: London, 1986.

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Table II. Calculated correction terms.

Atom	Coordination number	Correction term, kcal/mole
C	4	5.68
C	3	6.05
C	2	2.82
N	3 (planar)	10.04
N	3 (pyramidal)	2.08
N	2	7.27
N	1	1.42
O	2	-5.14
O	1	0.61

Table III. Gas phase heats of formation: test cases.

Molecule	Heats of formation, kcal/mole		
	Expt. ^a	Calc., corrected	Error
methyl acetate	-98.45	-97.04	1.41
ethylene glycol	-92.61	-85.62	6.99
1,4-dioxane	-75.48	-79.61	-4.13
diethyl ether	-60.25	-63.41	-3.16
acetamide	-56.96	-53.72	3.24
benzaldehyde	-8.77	-9.71	-0.94
furan	-8.34	-12.96	-4.62
vinyl chloride	8.91	3.41	-5.50
1,3,5-trinitrobenzene	14.9	18.23	3.3
pyridine	33.56	31.39	-2.17

^aJ. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman and Hall: London, 1986.