

Improved Correlation Between Theoretical and Experimental Determination of Heat of Formation of Some Aliphatic Nitro Compounds

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요약. 본 논문에서는 몇몇 사슬형 니트로 화합물의 실험적으로 측정된 생성열과 이론적으로 계산된 생성열과의 개선된 상관관계에 대해 보고하였다. 이 방법은 이전에 보고된 이론적인 방법을 따르고 있으며, 적당한 결합 파라미터를 도입하는 것으로 이전의 방법을 개선하였다. 실험적으로 측정된 값 그리고 이전의 이론값과 비교해본 결과 상당히 만족할 만한 결과를 보였다. 추후 적용 가능한 몇가지 점에 대해 지적하였다.

주제어: 생성열, 사슬형 니트로 화합물, 준이론적 방법

ABSTRACT. We present improved correlations between theoretical and experimental determination of heat of formation of some aliphatic nitro compounds. The method is based on a previously given theoretical procedure, which is ameliorate through the introduction of suitable bond parameters. The comparison with available experimental data and previous theoretical estimation show a quite satisfactory improvement. Some possible further extensions are pointed out.

Keywords: Heat of Formation, Aliphatic Nitro Compounds, Semi-Empirical Methods

INTRODUCTION

Alkanes can be converted into nitro derivatives by heating hydrocarbons at the vapor state with nitric acid vapors at a temperature around 420°C. Nitroalkanes are colourless liquids with a pleasant odor. They are scanty soluble in water but they can dissolve in the great majority of current organic solvents. They can be distilled without being decom-

posed and they can be employed as solid combustible while alkyl nitrates are explosive materials.

Chemical reactions can display complex, and even paradoxical, behavior. A certain experiment might yield one mixture of products under one set of conditions and a completely different mixture of products under a different set of conditions. In addition, many factors (temperature, reagent, concentrations, solvent and reaction time) can affect the

outcome of an experiment. Thus, understanding the relationship between these experimental factors and the outcome of chemical processes is a major goal of chemistry.

The way in which experimental conditions might favor one chemical reaction over another can be explained by invoking the notions of "kinetic control" and "thermodynamic control". A kinetically-controlled system is one where the outcome is determined by the relative rates of competing reactions. A thermodynamically-controlled system is one where the outcome is determined by the relative stability of competing products.

Chemical industry is concerned with improving the utility and value of raw materials by transforming them into chemical substances that may be either intermediates in a processing sequence or end product commodities. Since chemical reactions are characterized by a certain arrangement of atoms in the reactants and a different arrangement of the same atoms in the products, it is the task of the chemist to establish the conditions of temperature, pressure, and other constraints under which the reactant materials will preferentially rearrange to form the desired product molecules. A suitable thermodynamic analysis of the system may often provide considerable information on the proper conditions for obtaining the desired products. Reactions that cannot occur may be definitely eliminated, directing attention toward the feasible reactions. The fruitfulness of such a thermodynamic analysis will depend on the extent to which the basic thermodynamic properties of the substances involved are known, but even in the absence of complete data chemical thermodynamics permits intelligent speculation concerning the reaction products. As appropriate data become more abundant, the utility of this tool in modern research will increase even further.²

A number of methods for the estimation of thermochemical properties of organic compounds have been developed in recent years.³⁻⁵ The importance of reliable experimental basis for such methods is universally accepted among both scientists and engineers. A characteristic of many organic energetic compounds (*i.e.* explosives and propellants) is

the presence of the nitro group, $-\text{NO}_2$ ^{6,7}. It is typically linked to a carbon (nitroalkanes, nitroaromatics, nitroheterocycles), a nitrogen (nitramines), or an oxygen (nitrate esters). The nitro group has the desirable features that it increases the density of the compound and promotes the formation of very stable gaseous decomposition products (N_2 , CO , CO_2 , and H_2O), resulting in a greater energy release and pressure buildup per unit volume of material. The thermochemistry of nitro compounds has not been so intensively studied as that of other homologous series.⁸ Then, prediction of heats of formation of the aliphatic nitro compounds is necessary and also important since this thermodynamics property is fundamental for the explosive and propellant industries. Although experimental heats of formation of aliphatic nitro compounds are available in the standard literature, other ones are difficult to synthesize and some of them are highly unstable. Consequently, it would be useful to develop reliable theoretical methods to estimate the heats of formation of nitro derivatives. In case theoretical calculations and experimental data have a suitable degree of correlation, some explosive materials which are highly unstable and difficult to synthesize could be analyzed, and these data would be extremely useful to analyze the properties of those explosives.

The purpose of this work is to present an improved correlation method between theoretical and experimental determination of heat of formation of some aliphatic compounds. The paper is organized as follows: next section deals with the theoretical method based in a multivariable linear regression procedure improved via bond parameters. Then, we present results for a representative molecular set, comparing estimations with previous theoretical data, and discuss the numerical information. Finally, we point out the main conclusions derived from the present study and we suggest some possible further extensions.

CALCULATION METHOD

Although semi-empirical methods are especially designed to obtain enthalpy of formation of chemical compounds, in many cases the predicted values

cannot be compared with the experimental results because they present some serious drawbacks. In order to overcome these difficulties, Chen and Wu⁹ have developed several corrected equations between the experimental and AM1 and PM3 heats of formation for several aromatic nitro compounds by statistical considerations and these corrected equations have 95% predictive interval. Based on the successful correction of the aromatic nitro compounds, the authors deemed the application of multivariate linear fittings to the normal aliphatic nitro compounds could be worthy of further study. Thus, they selected 28 normal aliphatic nitro compounds, with methyl groups up to 4 and nitro groups up to 6, and performed AM1 and PM3 calculations.¹⁰ Calculated results were then corrected with the experimental data with various multilinear regression analyses. Correlations were evaluated by multivariable linear regression method, considering the number of nitro groups and the use the quadratic relations involving the number of carbon, hydrogen, nitrogen, and oxygen atoms. Results indicated very precise correlations. Based on these correlations, heats of formation of the set of 28 aliphatic nitro hydrocarbons could be predicted at 95% predictive interval without experimental analysis.

However, we deem there is room to introduce some additional correction terms which can improve final results. In fact, in some previous papers, two of us (PD and FAC) have demonstrated that taking into account the presence of different chemical bonds to predict physical chemical properties final estimations can be ameliorated significantly when using this sort of approach.¹¹⁻¹⁵ This approach can be justified from the Cioslowski's remark¹⁶ on the need to insert a correction term in this sort of relationships to take into account the electron correlations effects associated with bond formation.

Chen *et al.*¹⁰ have employed several multilinear models to predict improved heat of formation of nitro aliphatic compounds. The general formulation was

$$\Delta H_f^\circ(\text{theor.}) = a\Delta H_f^\circ(\text{semiemp.}) + \sum_i^{atoms} a_i n_i + b$$

where a , b and $\{a_i\}$ are regression coefficients and n_i is

the number of i -atoms. $\Delta H_f^\circ(\text{theor.})$ is the theoretical estimation of the enthalpy of formation and $\Delta H_f^\circ(\text{semiemp.})$ is the heat of formation calculated from a given semiempirical method (PM3 and AM1 in this case).

Here we propose the following generalization of the above equation

$$\Delta H_f^\circ(\text{theor.}) - a\Delta H_f^\circ(\text{semiemp.}) + \sum_i^{atoms} a_i n_i + \sum_{i-j}^{atoms} a_{i-j} n_{i-j} + b \quad (2)$$

where n_{i-j} is the number of $i-j$ bonds and $\{a_{i-j}\}$ are the corresponding regression coefficients.

In order to make a direct comparison with previous results, we have chosen the same molecular set of 28 nitro aliphatic hydrocarbons as that employed by Chen *et al.*¹⁰ Besides, to keep at a minimum the number of parameters we have also taken into account the number of C-C chemical bonds. We have also tested another generalization of Eq. (2) resorting to a quadratic form, such as

$$\Delta H_f^\circ(\text{theor.}) - \Delta H_f^\circ(\text{semiemp.}) + \sum_i^{atoms} (a_i n_i + A_i n_i^2) + \sum_{i-j}^{bonds} (a_{i-j} n_{i-j} - A_{i-j} n_{i-j}^2) \quad (3)$$

where $\{A_i\}$ and $\{A_{i-j}\}$ are the regression coefficients associated with the square numbers of atoms and bonds, respectively. We have also shown that the use of this second-order relationships sometimes improves markedly the estimations.¹⁷⁻²¹ In fact, the use of just linear fitting relationships restricts regression analysis considerably. Many correlations, particularly when involving molecules of different size, need not be linear. But even if we have molecules of the same or similar size, a quadratic or/and cubic regression may result in a better description of the relationship between property and molecular descriptor than a simple linear model. In general, one should test single or and multiple descriptor regression for quadratic dependence and, if warranted, for higher polynomial relationships or other functional dependence.²²

RESULTS AND DISCUSSION

In *Table 1* we present the molecular set together

Table 1. Enthalpy of formation (kcal mol) of aliphatic nitro derivatives. Data from Ref. 10

Molecule	Exp.	AM1	PM3	Eq.(9)	Eq.(13)	Eq.(10)	Eq.(14)
1. Nitromethane	-12.2	-9.9	-15.9	-17.8	-15.0	-15.4	-14.4
2. Dinitromethane	-14.3	2.9	-11.9	-12.7	-12.2	-11.8	-12.6
3. Trinitromethane	-3.2	25.0	-4.7	-1.3	-2.0	-4.2	-2.8
4. Tetranitromethane	18.5	54.8	13.0	22.1	17.6	17.8	18.2
5. Nitroethane	-23.5	-16.8	-21.4	-25.2	-23.9	-23.4	-23.5
6. 1,1-Dinitroethane	-24.1	-2.6	-17.4	-20.7	-21.4	-20.9	-22.2
7. 1,2-Dinitroethane	-22.9	-11.5	-20.0	-24.8	-23.5	-22.8	-23.8
8. 1,1,1-Trinitroethane	-12.4	22.8	-6.7	-10.8	-13.4	-13.4	-12.4
9. 1,1,2-Trinitroethane	-	7.5	-13.1	-17.7	-14.0	-17.9	-15.1
10. Hexanitroethane	35.8	92.9	46.0	31.5	36.1	36.6	35.8
11. 1-Nitropropane	-29.7	-23.7	-26.3	-31.5	-31.1	-30.3	-30.4
12. 2-Nitropropane	-33.9	-21.6	-27.1	-30.6	-30.3	-30.9	-31.1
13. 1,1-Dinitropropane	-25.9	-9.2	-22.0	-27.3	-28.1	-27.8	-28.8
14. 1,2-Dinitropropane	-	-16.6	-25.7	-30.7	-30.2	-30.5	-31.5
15. 1,3-Dinitropropane	-31.6	-21.5	-26.4	-32.9	-31.9	-30.9	-32.0
16. 2,2-Dinitropropane	-27.0	-4.8	-19.9	-25.3	-27.0	-26.4	-27.4
17. 1,1,1-Trinitropropane	-18.4	16.4	-9.7	-17.9	-19.3	-19.7	-17.7
18. 1,1,2-Trinitropropane	-	2.8	-16.7	-24.1	-20.6	-24.7	-21.2
19. 1,2,2-Trinitropropane	-	4.1	-16.3	-23.6	-20.4	-24.4	-21.0
20. 1,2,3-Trinitropropane	-	-8.5	-20.7	-29.3	-22.9	-27.5	-23.6
21. 1-Nitrobutane	-34.4	-30.4	-31.6	-37.4	-37.3	-37.0	-36.4
22. 2-Nitrobutane	-39.1	-28.2	-31.9	-36.4	-36.3	-37.2	-36.6
23. 1,1-Dinitrobutane	-34.1	-16.0	-27.2	-33.4	-33.6	-34.7	-34.3
24. 1,2-Dinitrobutane	-	-22.9	-29.9	-36.6	-36.1	-36.6	-36.5
25. 1,3-Dinitrobutane	-	-26.0	-31.9	-37.7	-37.3	-38.0	-38.2
26. 1,4-Dinitrobutane	-38.9	-28.8	-32.8	-39.2	-38.5	-38.6	-39.0
27. 2,2-Dinitrobutane	-	-9.4	-21.8	-30.4	-31.7	-30.9	-30.2
28. 2,3-Dinitrobutane	-	-19.0	-28.8	-34.7	-34.6	-35.9	-35.6
Average absolute deviation	-	19.0	5.5	2.2	1.4	1.4	1.1

with available experimental data and some previous theoretical results.

An inspection of results derived from direct calculations from AM1 and PM3 semiempirical methods reveals that the second is procedure clearly superior to the first one. However, both methods overestimate enthalpy of formation and absolute deviations are rather large (*i.e.* 19.0 and 5.5 kcal/mol, respectively). Evidently, no confident predictions can be made from these two methods, since average experimental deviations are about 2 kcal/mol. Then, it is necessary to resort to a more reliable procedure.

The regression equations for linear (Eq. 2) and quadratic (Eq. 3) approximations obtained from the fitting to the experimental data yield the estimations of heat of formation displayed in Table 2. A

complete listing of the numerical coefficients corresponding to the fitting relationships is available upon request to the corresponding author.

The present correction method yields more confident predictions, which in general present average absolute deviations rather similar to the experimental uncertainties. In fact, only linear equation based on AM1 method gives a relatively large average absolute deviation larger than 2 kcal/mol. Specially noticeable are the improvements obtained when passing from linear to quadratic fitting equations.

Chen *et al.* have pointed out that hydrogen atom effect must be excluded or be taken into account in an inverse way into the regression equations on the basis of the comparison of the scatter plots among variables.¹⁰ Thus we have determined regression

Table 2. Heats of formation (kcal mol) of 28 aliphatic nitro derivatives calculated in this work

Molecule	Exper.	Eq.(2) AMI	Eq.(3) AMI	Eq.(2) PM3	Eq.(3) PM3
1.	-12.2	-17.8	-13.7	-14.5	-14.0
2.	-14.3	-12.5	-11.6	-11.3	-11.5
3.	-3.2	-1.2	-4.0	-5.1	-1.2
4.	18.5	15.2	17.3	11.0	15.0
5.	-23.5	-25.1	-23.9	-22.8	-24.3
6.	-24.1	-18.9	-21.1	-19.6	-22.4
7.	-22.9	-24.7	-25.1	-22.1	-24.1
8.	-12.4	-5.5	-11.1	-10.2	-11.0
9.	-	-15.4	-23.9	-16.2	-13.7
10.	35.8	30.9	36.3	37.8	36.4
11.	-29.7	-32.4	-31.6	-30.6	-31.3
12.	-33.9	-31.1	-31.3	-31.4	-32.0
13.	-25.9	-26.0	-25.9	-25.9	-25.9
14.	-	-30.9	-31.6	-30.7	-32.6
15.	-31.6	-34.0	-32.8	-31.3	-33.1
16.	-27.0	-23.2	-27.0	-25.2	-28.4
17.	-18.4	-12.4	-20.2	-16.1	-17.6
18.	-	-21.3	-30.3	-22.8	-21.1
19.	-	-20.5	-29.5	-22.4	-20.9
20.	-	-28.7	-36.3	-26.6	-23.6
21.	-34.4	-39.6	-37.1	-38.9	-35.7
22.	-39.1	-38.2	-36.9	-39.1	-35.9
23.	-34.1	-33.3	-34.7	-35.3	-34.7
24.	-	-37.8	-36.3	-37.8	-36.9
25.	-	-39.8	-36.8	-39.7	-38.7
26.	-38.9	-41.6	-37.1	-40.5	-39.6
27.	-	-29.0	-32.3	-30.1	-30.5
28.	-	-35.2	-35.5	-36.8	-36.0
Average absolute deviation	-	3.2	1.5	2.1	1.5

equations excluding hydrogen atoms and the results are given in Table 3 for molecules with available experimental data.

We note that results do not improve when deleting H atoms effect in the regression equations, so that we deem they must be taken into account within the present calculation scheme. The comparison between previous¹⁰ and present calculations shows they are of comparable quality, save the predictions derived from Eq. (14) in Ref. 10, which are better than present ones based on our Eq. (3). However, differences in average absolute deviations are not so important (1.1 kcal/mol vs 1.5 kcal/mol) since experimental uncertainties are larger than these values (*i.e.* 2 kcal/mol).

The main advantage on resorting to the employment of our approximation scheme instead the previous one rests upon the fact that a correction term based on chemical bonds is more natural to the chemical understanding than another one based on the inverse effect of the hydrogen atom presence. In fact, the naïve chemical intuition feels at ease when considering chemical phenomena in terms of atoms and bonds, while it results rather awkward to rationale them in terms of an inverse effect due to the presence of a certain kind of atom/s. Since both approximations give somewhat satisfactory predictions of heats of formation of the present molecular set, we consider this method is sound to perform this sort of thermodynamics calculations.

Table 3. Heats of formation (kcal mol) for 19 aliphatic nitro compounds predicted without hydrogen atom effect

Molecule	Exper.	Eq.(2) AM1	Eq.(3) AM1	Eq.(2) PM3	Eq.(3) PM3
1	-12.2	-17.8	-15.2	-14.5	-12.4
2	-14.3	-12.5	-11.5	-11.3	-10.8
3	-3.2	-1.2	-2.4	-5.0	-2.3
4	18.5	15.2	16.7	11.0	13.3
5	-23.5	-25.1	-24.1	-22.8	-24.0
6	-24.1	-18.9	-20.7	-19.6	-22.0
7	-22.9	-24.7	-24.2	-22.1	-24.0
8	-12.4	-5.5	-10.7	-10.1	-10.8
10	35.8	30.9	36.3	37.8	36.9
11	-29.7	-32.4	-31.2	-30.6	-31.8
12	-33.9	-31.1	-30.7	-31.4	-32.5
13	-25.9	-26.0	-28.7	-27.1	-29.1
15	-31.6	-34.0	-32.4	-31.2	-32.9
16	-27.0	-23.2	-27.0	-25.1	-27.5
17	-18.4	-12.4	-20.0	-16.0	-16.0
21	-34.4	-39.6	-36.4	-38.8	-36.5
22	-39.1	-38.2	-36.1	-39.0	-36.8
23	-34.1	-33.3	-34.9	-35.2	-33.4
26	-38.9	-41.6	-37.9	-40.4	-38.8
Average absolute deviation	-	3.2	1.7	2.2	1.7

CONCLUSIONS

We have presented the results of heats of formation of 28 aliphatic nitro compounds calculated on the basis of modified AM1 and PM3 semiempirical predictions. The comparison of theoretical values with available experimental data of 19 molecules gives absolute average deviations smaller than usual experimental uncertainties, so that it leads us to make confident true predictions for those molecules whose enthalpies of formation are unknown up to now. Comparison of present results with those derived from a closely related approximation scheme reveal a similar quality of both multivariate linear and quadratic regression methods. However, present equations are amenable of a more transparent and direct chemical interpretation. Present calculations also show the convenience of resorting to polynomial orders larger than one for fitting equations since final results improve in a marked manner to predict thermodynamics properties. Although these findings have been also found previously, we deem that some complementary calculations on different thermodynamical properties and other molecular

sets should be made in order to state more definitive conclusions. Work along these lines are at present under developments in our laboratories and results will be presented elsewhere in the forthcoming future.

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