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On the heat of formation of nitromethane

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Two experimental values (−19.3 ± 0.3 and −17.8 ± 0.1 kcal/mol) for the gas phase heat of formation ($\Delta_f H_g^0$) (298k) of nitromethane have been reported. Although these values differ by only 1.5 kcal/mol, substantially greater differences in theoretical and experimental results occur when these differing values are used to calculate thermodynamic properties. This is especially evident when these two values for the $\Delta_f H_g^0$ of nitromethane are used to calculate thermodynamic properties of polynitro compounds. For example, when density functional theory (DFT) is coupled with the use of isodesmic reactions, the $\Delta_f H_g^0$ of octanitrocubane is calculated to be 160.6 or 172.6 kcal/mol, depending on which value is used. It should also be appreciated that several computational theories depend upon having access to reliable experimental data for testing and development. We have examined this discrepancy using several computational models and several levels of theory. Our results coupled with a comprehensive review of the literature support the lower (−19.3 ± 0.3 kcal/mol) experimental value. This is problematic because the higher value (−17.8 ± 0.1 kcal/mol) has been used in the development and/or testing of several semiempirical quantum mechanical models as well as *ab initio* Gaussian theory (G2 and G3). Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: nitromethane; gas phase heat of formation; density functional theory; *ab initio* theory; group additivity approach

INTRODUCTION

Nitromethane (CAS number 75-52-5) is a relatively common organic solvent. It has been used as a fuel in auto racing and as an explosive.[1–3] It is also used as an intermediate in the manufacture of drugs, high explosives, pesticides, and other useful materials. The liquid explosive PLX (Pictanny liquid explosive) is a mixture composed of 95% nitromethane and 5% ethylenediamine.[3] Nitromethane is prepared by the reaction between sodium nitrite and sodium chloroacetate.[4]

As a widely used article of commerce, the chemical and physical properties of nitromethane have been well studied. Nevertheless, there is some discrepancy regarding the gas phase heat of formation ($\Delta_f H_g^0$) (298k) of this compound. A value of −19.3 ± 0.3 kcal/mol has been reported by Knobel *et al.*[5] This is the value listed by the NIST WebBook.[6] The other value of −17.8 ± 0.1 kcal/mol is listed in Pedley's *Thermochemical Data of Organic Compounds*,[7] a value based on and statistically indistinguishable from the value of −17.86 kcal/mol reported by McCullough *et al.*[8]

The two reported experimental values for the $\Delta_f H_g^0$ of nitromethane differ by only 1.5 kcal/mol. Nevertheless, substantial differences in theoretical and experimental results occur when these differing values are used to calculate thermodynamic properties. This is especially evident when these two values for the $\Delta_f H_g^0$ of nitromethane are used to calculate thermodynamic properties of polynitro compounds. For example, when density functional theory (DFT) is coupled with the use of isodesmic reactions, the $\Delta_f H_g^0$ of octanitrocubane is calculated to be 160.6 or 172.6 kcal/mol, depending on which value for the $\Delta_f H_g^0$ of nitromethane is used.[9,10]

Also of concern is the fact that the $\Delta_f H_g^0$ of nitromethane is used in the training set and/or test set (or reference set) during the development of semiempirical quantum mechanical models. For example, Dewar and Stewart and their associates[11–13] used the value of about −17.8 kcal/mol (actually −17.7 and −17.9 kcal/mol) for the $\Delta_f H_g^0$ of nitromethane as one of many experimental values for a large number of compounds in the development, parameterization, and testing of semiempirical models, AM1, PM3 and, most recently, PM6 and RM1.[14] Similarly, this value was also one of many that were used to develop and/or test Gaussian 2 (G2) and Gaussian 3 (G3). G1, G2, and G3[15–21] are very robust multilevel *ab initio* methods that are combined with the use of an extrapolation equation that is empirically defined and parameterized to reproduce results (i.e., $\Delta_f H_g^0$ and other properties) for individual compounds included in a test set of molecules. It is then assumed that these models and methods will also be able to calculate, with some degree of accuracy, reasonable values for compounds (i.e., 'unknowns') that were not used in their development. Thus, incorrect data used in parameterization will be one source of error in such models. Even if the contribution to model error was minimal in such circumstances, the use of an incorrect value in the test set would provide an incorrect assessment of the accuracy of the model as it pertains to nitromethane.

Not all quantum mechanical procedures to calculate $\Delta_f H_g^0$ of nitromethane used −17.8 kcal/mol as a reference value. Rice *et al.*[22] used the value of −19.3 kcal/mol as the reference $\Delta_f H_g^0$ value for nitromethane in investigations in which an atom equivalent scheme was used to convert DFT energies to heats of

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formation for the calculation of $\Delta_f H_g^0$ values for a wide variety of nitrogen-containing compounds. The point here is that investigators must have confidence that they are using the most reliable experimental data available to develop and/or test the quantum mechanical models under consideration. Furthermore, this is problematic when two or more reported experimental values exist for any given compound.

In a more general sense, it is always important to be confident of $\Delta_f H_g^0$ values because these values may be used to calculate other important and useful thermodynamic properties. For example, the sum of the heats of formation of products ($\Sigma\Delta_f H_{g,P}^0$) minus the sum of the heats of formation of the reactants ($\Sigma\Delta_f H_{g,R}^0$) of a chemical reaction may be used to calculate the heat of reaction ($\Delta_r H^0$) as follows:

$$\Delta_r H^0 = \Sigma\, \Delta_f H_{g,P}^0 - \Sigma\, \Delta_f \mathrm{H}_{g,R}^0$$

This value ($\Delta_r H^0$) can subsequently be used to calculate the equilibrium constant for a reaction using the following relationships:

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta S_r^o$$

$$\Delta_r G^o = -\mathrm{RTlnK}$$

As noted by Cohen and Benson,[23] a relatively small error in $\Delta_f H_g^0$ can have important consequences. For a general reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}$$

An error in the calculation of $\Delta_r H^0$ of only 1 kcal/mol results in a substantial (greater than fivefold) change in the equilibrium constant. In turn, this results in poorly predicted parameters such as reaction yield, concentration of reactants and products at equilibrium, and rate of reaction.

When they exist, it is clearly important to address such inconsistencies in the literature. Computational methods have been used to lend support to experimental values for $\Delta_f H_g^0$ values when two or more different experimental values have been reported. For example, Smith *et al.*[24] demonstrated the usefulness of multilevel *ab initio* molecular orbital theory (i.e., G2) to obtain a reliable $\Delta_f H_g^0$ value of 20.6 ± 2.4 kcal/mol for methanimine at a time when this value was in dispute. Similarly, Saraf *et al.*[25] used a semiempirical model, a group additivity approach and several density functional and *ab initio* models coupled with two isodesmic reactions to assess the $\Delta_f H_g^0$ of hydroxylamine, recommending use of a computed $\Delta_f H_g^0$ of −11.4 kcal/mol, a value that is statistically indistinguishable from the reported experimental value of −12.0 kcal/mol.

We have also taken a computational approach in an effort to determine if our computed results support one or the other of the experimentally determined values for the $\Delta_f H_g^0$ of nitromethane. In our studies, we have used isodesmic and hydrogenation reactions coupled with DFT using several basis sets.[26,27] Semiempirical models[11–14] were also cautiously used as was a modification of Benson's group additivity approach.[23,28,29]

To determine if a consensus can be reached regarding the most accurate value for this compound, this manuscript also provides a comprehensive survey and review of the available literature, both computational and experimental, regarding the $\Delta_f H_g^0$ of nitromethane.

Computational methods

Density functional theory

DFT[26,27] coupled with the use of four isodesmic reactions (Rxns 1 to 4) and four hydrogenation reactions (Rxns 5 to 8)

Rxn 1 $CH_2(NO_2)_2 + CH_4 \rightarrow 2\ CH_3NO_2$
Rxn 2 $CH_2(NO_2)_2 + CH_2(NO_2)_2 \rightarrow CH(NO_2)_3 + CH_3NO_2$
Rxn 3 $CH(NO_2)_3 + 2\ CH_4 \rightarrow 3\ CH_3NO_2$
Rxn 4 $C(NO_2)_4 + 3\ CH_4 \rightarrow 4\ CH_3NO_2$
Rxn 5 $CH_3 - CH_3 + 2\ HNO_2 \rightarrow H_2 + 2\ CH_3NO_2$
Rxn 6 $CH_3 - CH(NO_2)_2 + H_2 \rightarrow 2\ CH_3NO_2$
Rxn 7 $CH_4 + HNO_2 \rightarrow H_2 + CH_3NO_2$
Rxn 8 $CH_2(NO_2)_2 + CH_3CH_2CH_3 + H_2 \rightarrow CH_3 - CH_3 + 2\ CH_3NO_2$

was used to calculate the $\Delta_f H_g^0$ of nitromethane. The DFT-B3LYP method in combination with the 6-31G* basis set is a relatively modest level of computational theory. However, as noted by Zhang *et al.*[10] several investigations have shown that this level of theory often predicts accurately the energies, molecular structures, and vibrational energies of compounds that are close to their experimental values. Thus, the DFT-B3LYP method in combination with the 6-31G* basis set was used. Additionally, four other larger basis sets (6-31 G**, 6-31+G*, 6-311 G*, and 6-311+G**) were used in this study.

Heats of reaction ($\Delta_r H_{298}^0$) were calculated using the following equation:

$$\Delta_r H_{298}^0 = \Sigma\, \Delta_f H_{g,P}^0 - \Sigma\, \Delta_f H_{g,R}^0$$

where $\Sigma\Delta_f H_{g,P}^0$ and $\Sigma\Delta_f H_{g,R}^0$ are the sums of the heats of formation of the products and the reactants in each reaction, respectively. In these equations, the $\Delta_f H_g^0$ for nitromethane was treated as an unknown and the experimental $\Delta_f H_g^0$ values for each of the other molecules were from References [6,7,29] and [30]. The value for $\Delta_r H_{298}^0$ was determined by computation using the following equations:

$$\Delta_r H_{298}^0 = \Delta E_{298} + \Delta(PV)$$

$$\Delta_r H_{298}^0 = \Delta E_0 + \Delta \mathrm{ZPE} + \Delta H_T + \Delta nRT$$

where ΔE_0 is the total electronic energy change at 0 K between products and reactants of the isodesmic and hydrogenation reactions that were used. The change in zero point energies is represented by ΔZPE and H_T is the thermal correction factor required to express ΔE at 298.15 K instead of 0 K. For reactions in the gas phase, $\Delta(PV) = \Delta nRT$. For the reactions used in this study, $\Delta n = 0$, thus $\Delta(PV) = 0$. Total electronic energy at 0 K (E_0), ZPE and the values (translational enthalpy, rotational enthalpy, and vibrational enthalpy) required to compute H_T were calculated using the Spartan 06 (Wavefunction, Inc., Irvine, CA) suite of programs. Vibrational frequency scaling factors of 0.9603, 0.9603, 0.9600, 0.9663, and 0.9600 were used for calculations involving the 6-31G*, 6-31 G**, 6-31+G*, 6-311 G*, and 6-311+G** basis sets, respectively. Minimized structures exhibited no imaginary frequencies.

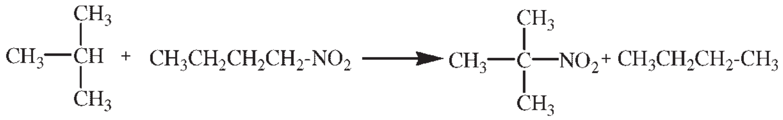
For this study, it was important to assess the general ability of theory to accurately predict the $\Delta_f H_g^0$ values of nitroalkanes. Thus, the $\Delta_f H_g^0$ values of several nitroalkanes structurally similar to nitromethane were calculated using three isodesmic and three hydrogenation reactions, control Rxns 1–6.

Control Rxn 1 □ $CH_3\text{-}CH_3 + HNO_2 \longrightarrow H_2 + CH_3CH_2\text{-}NO_2$

Control Rxn 2□□$CH_3CH_2CH_3 + HNO_2 \longrightarrow H_2 + CH_3CH_2CH_2\text{-}NO_2$

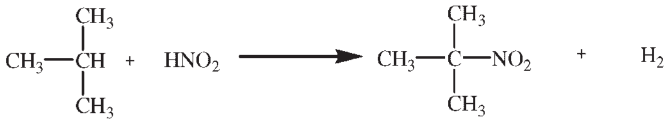
Control Rxn 3□□$CH_3CH_2CH_2CH_3 + HNO_2 \longrightarrow H_2 + CH_3CH_2CH_2CH_2\text{-}NO_2$

Control Rxn 4



$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{CH}} + CH_3CH_2CH_2CH_2\text{-}NO_2 \longrightarrow CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}NO_2 + CH_3CH_2CH_2\text{-}CH_3$$

Control Rxn 5



$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{CH}} + HNO_2 \longrightarrow CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}NO_2 + H_2$$

Control Rxn 6 $CH_3CH_2CH_2CH_2\text{-}NO_2 + CH_3CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_3 + CH_3CH_2CH_2\text{-}NO_2$

Semiempircal theory

Semiempirical models are parameterized to provide heat of formation as an output value instead of the total electronic energy term as occurs in *ab initio* and DFT calculations. Several semiempirical models (MNDO, AM1, PM3, PM6, and RM1) were used to calculate the heat of formation of nitromethane. Results were quite variable between models, but consistent with results of others. MNDO, AM1, PM3 and RM1 semiempirical calculations were performed using the Spartan 06 (Wavefunction, Inc.) suite of programs. PM6 calculations were performed using MOPAC 2007[14].

In addition to using output values for $\Delta_f H_g^0$ in semiempirical models, one may sometimes *cautiously* use calculated output values for $\Delta_f H_g^0$ values coupled with isodesmic reactions to calculate the heat of reaction ($\Delta_r H_{298}^0$) and, subsequently, (re)calculate the $\Delta_f H_g^0$ of an unknown (in this case nitromethane) using experimentally derived $\Delta_f H_g^0$ values of the other components of the isodesmic reaction.

In such procedures $\Delta_r H_{298}^0$ is calculated by the following:

$$\Delta_r H_{298}^0 = \Sigma\,\Delta_f^{\text{calc}} H_P^0 - \Sigma\,\Delta_f^{\text{calc}} H_R^0$$

where $\sum \Delta_f^{\text{calc}} H_P^0$ and $\sum \Delta_f^{\text{calc}} H_R^0$ are the sums of the semiempirically calculated output values for heats of formation of the products and reactants, respectively. Once $\Delta_r H_{298}^0$ has been calculated, the heat of formation of nitromethane can be (re)calculated using the following:

$$\Delta H_{298}^0 = \Sigma\,\Delta_f^{\text{exp't}} H_P^0 - \Sigma\,\Delta_f^{\text{exp't}} H_R^0$$

where $\sum \Delta_f^{\text{exp't}} H_P^0$ and $\sum \Delta_f^{\text{exp't}} H_R^0$ are of the sums of the experimental values for the heats of formation of products and reactants, respectively. In this reaction, the experimental $\Delta_f H_g^0$ value for nitromethane is treated as the sole unknown and is calculated. In such procedures, one makes the assumption that deviation (i.e., error) of semiempirically computed $\Delta_f H_g^0$ values from experimental $\Delta_f H_g^0$ values is systematic between molecules used in such equations and thus error is cancelled in these calculations.

Of the semiempirical models tested, the PM3 model calculated $\Delta_f H_g^0$ values for methane, nitromethane, dinitromethane, and trinitromethane, to within 5 to 6 kcal/mol of reported experimental values.[9] The PM3 model has also been shown to calculate with a fair degree of accuracy the heats of formation of several nitrogen-containing high explosives.[9,31] Because of this, the PM3 model was used to calculate the $\Delta_f H_g^0$ of nitromethane using the four isodesmic equations described in Rxns 1 to 4.

Hydrogenation reactions were not used in these analyses because the PM3 model calculates a $\Delta_f H_g^0$ for H_2 that is more than 13 kcal/mol less than the value of 0 kcal/mol, the $\Delta_f H_g^0$ value of an element in its most stable form.

Group additivity and the difference method

The group additivity approach[23,28,29] in a remarkably straight forward manner accurately predicts $\Delta_f H_g^0$ and other physical properties of a wide variety of compounds and $\Delta_f H_g^0$ values of several simple nitroalkanes are accurately predicted by this approach.[29] As accurate as this approach is for many relatively simple (and some not so simple compounds), it is interesting to note that the properties of the simplest nitroalkane, nitromethane was not included in Benson's original work, nor is the $\Delta_f H_g^0$ value of this compound calculated by the group additivity applet maintained by the NIST.[32] Ironically, $\Delta_f H_g^0$ values of C1 compounds are sometimes among the more difficult to address using this method. The $\Delta_f H_g^0$ values for nitroethane, 1-nitropropane, and 1-nitrobutane have, however, been estimated by this method and agree very well with experimental values.[29] Interestingly, the $\Delta_f H_g^0$ value of nitromethane can be calculated by subtracting from the $\Delta_f H_g^0$ values of nitroalkanes a group equivalent value of -5.0 kcal/mol for each methylene group (—CH_2—) present in nitroethane, 1-nitropropane, and 1-nitrobutane. This approach is referred to by Cohen and Benson[23] as the difference method.

Weizmann-1 theory

Weizmann-1 (W1) is a computationally intensive and highly accurate multilevel *ab initio* method that can be used to compute total atomization energies (TAEs) and $\Delta_f H_g^0$ of small compounds composed of first and second row elements.[33–35] The $\Delta_f H_g^0$ of nitromethane was calculated at the University of Minnesota Supercomputing Institute using Gaussian 03 software. The keyword used to initiate a W1 calculation in Gaussian 03 is W1U.

RESULTS AND DISCUSSION

Density functional theory/isodesmic and hydrogenation reactions

Gas phase heat of formation values for nitromethane calculated using isodesmic and hydrogenation reactions are presented in

Table 1. Heat of formation values ($\Delta_f H_g^0$) (298k) in kcal/mol for nitromethane calculated using density functional theory (B3LYP) and several basis sets coupled with the use of isodesmic and hydrogenation reactions (Rxns 1–8)

Method	Basis Set	Rxn 1	Rxn 2	Rxn 3	Rxn 4	Rxn 5	Rxn 6	Rxn 7	Rxn 8	Mean ± SD
B3LYP	6-31 G*	−19.3	−18.7	−19.5	−18.3	−21.2	−19.9	−20.6	−20.2	−19.7 ± 1.0
	6-31 G**	−19.6	−18.8	−19.5	−18.2	−19.2	−19.5	−18.7	−20.0	−19.2 ± 0.6
	6-31+G*	−20.7	−18.5	−21.4	−20.9	−20.9	−21.5	−20.0	−21.9	−20.7 ± 1.1
	6-311 G*	−19.4	−18.5	−19.8	−18.8	−21.0	−19.6	−20.6	−20.4	−19.8 ± 0.9
	6-311+G**	−20.8	−17.4	−21.2	−20.6	−18.0	−21.2	−18.2	−21.8	−19.9 ± 1.7
PM3	—	−19.5	−21.7	−18.7	−10.8[a]	—	—	—	—	−20.0 ± 1.6

[a] This value was not included in calculating mean ± SD. Refer to text for details.

Table 1. Clearly, the calculated $\Delta_f H_g^0$ values tended to cluster nearer the −19.3 kcal/mol experimental value rather than the −17.8 kcal/mol experimental value.

Because two reported experimental values for the $\Delta_f H_g^0$ of nitromethane are being compared in our investigation it would be logical to expect that the most accurate or correct value would be the one that, when used in conjunction with isodesmic and hydrogenation reactions, results in calculated $\Delta_f H_g^0$ values that are most similar to experimental $\Delta_f H_g^0$ values for the other components of the reactions that are used. Results comparing experimental and calculated $\Delta_f H_g^0$ values for all compounds in Rxns 1–8 are presented in Table 2. Calculated $\Delta_f H_g^0$ values in Table 2 were determined at the DFT B3LYP/6-31 G** level of theory. Results demonstrated that, in most cases, the calculated $\Delta_f H_g^0$ values of the other components in these reactions were most similar to experimental $\Delta_f H_g^0$ values when a $\Delta_f H_g^0$ value of −19.3 kcal/mol for nitromethane was used. To express these data in a more quantitative manner, the mean absolute error (MAE) was calculated. When the −19.3 kcal/mol value was used, an MAE of only 0.9 kcal/mol was calculated in contrast to an MAE of 2.2 kcal/mol calculated when the −17.8 kcal/mol value was used in these isodesmic and hydrogenation reactions.

The general ability of DFT (in conjunction with isodesmic and hydrogenation reactions) to accurately calculate $\Delta_f H_g^0$ values of nitroalkanes, other than nitromethane, was also determined (Table 3) using a series of control reactions (control Rxns 1–6). In these studies, the experimental values to which computed results were compared have reported error (±SD) values ranging from ±0.2 to ±0.8 kcal/mol. MAE values for computed data were between 0.8 and 2.1 kcal/mol. These results confirm the general effectiveness and accuracy of this approach for the calculation of $\Delta_f H_g^0$ values for nitroalkanes.

As noted above, the approaches presented here using DFT coupled with isodesmic and hydrogenation reactions support the experimental value of −19.3 ± 0.3 kcal/mol for the heat of formation of nitromethane. This level of theory can be viewed as moderately robust. Although an isodesmic approach should compensate for systematic errors in DFT calculations, one also needs to take into account the fact that the experimental $\Delta_f H_g^0$ values used in isodesmic reactions have the potential to introduce error into these calculations. For example, the experimental $\Delta_f H_g^0$ value of dinitromethane is reported as −14.1 kcal/mol, but the reported error is substantial, ±1.0 kcal/mol. Because of this, we elected to use several isodesmic and hydrogenation reactions composed of a variety of different compounds such that no single experimental value would dramatically bias results for the entire set of reactions. It should also be noted that the experiments illustrated in Table 2 were designed specifically as an internal control. In Table 2, it was shown that when DFT (coupled with four isodesmic reactions and four hydrogenation reactions) was used, the $\Delta_f H_g^0$ values of the nine compounds (other than nitromethane) used to construct these reactions were more accurately predicted when −19.3 kcal/mol was used as the $\Delta_f H_g^0$ value for nitromethane.

Semiempirical theory

Heat of formation values for nitromethane calculated using semiempirical models MNDO, AM1, PM3, PM6, and RM1 are 3.3, −9.9, −15.9, −16.3, and −12.4, respectively. Three (MNDO, AM1, and RM1) of the five models predict $\Delta_f H_g^0$ values that are considerably greater than either of the two experimental $\Delta_f H_g^0$ values that have been reported. PM3 and PM6 predict $\Delta_f H_g^0$ values that are within 2.0 kcal/mole of the higher experimental value. PM3 was also used to calculate $\Delta_f H_g^0$ of nitromethane using four isodesmic reactions (Rxns 1 to 4) as shown in Table 1. The mean for Rxns 1 to 3 was −20.0 ± 1.6 kcal/mol. The computed $\Delta_f H_g^0$ value using Rxn 4 was not used to determine this mean as it is considerably greater than either of the two reported experimental values. This occurred because the PM3 output value (6.4 kcal/mol *vs.* an experimental value of 19.7 kcal/mol) for tetranitromethane does not predict very accurately the $\Delta_f H_g^0$ for this compound.

The PM3 model overestimates $\Delta_f H_g^0$ values of several monosubstituted nitroalkanes, but it does so on a very consistent basis. This is demonstrated in Fig. 1 in which the ability of PM3 theory to calculate $\Delta_f H_g^0$ of the C1 to C4 *n*-nitroalkanes is presented and compared to experimental data. This consistency in overestimation is the reason that these data can be used to calculate $\Delta_f H_g^0$ values using isodesmic equations. Results using the PM3 model with control isodesmic reactions are presented in Table 3. As mentioned above, the PM3 model was not used in hydrogenation reactions because this model poorly predicts the $\Delta_f H_g^0$ value for hydrogen. Of all of the computational studies presented or reviewed herein, we would note that semiempirical theory is regarded as the least robust with regard to supporting highly accurate heats of formation. It should also be noted that results obtained using semiempirical (PM3) theory were included with results obtained using density functional theory in Table 1 and Table 3 as a matter of convenience to facilitate presentation and comparison of results.

Table 2. Comparison of heat of formation values ($\Delta_f H_g^0$) (298k) in kcal/mol of all compounds in isodesmic and hydrogenation reactions (Rxns 1–8) calculated using both experimental heat of formation values that have been reported for nitromethane (DFT B3LYP 6-31 G** level of theory).[a]

	Exp't $\Delta_f H_g^0$	Theory $\Delta_f H_g^0$	Exp't-theory	Theory $\Delta_f H_g^0$	Exp't-theory
		Exp't = −19.3	Exp't = −19.3	Exp't = −17.8	Exp't = −17.8
Rxn 1					
Nitromethane	(−19.3 or −17.8)	−19.6	+0.3	−19.6	+1.8
Dinitromethane	−14.1	−14.1	0.0	−11.1	−3.0
Methane	−17.89	−17.85	−0.04	−14.85	−3.04
Rxn 2					
Nitromethane	(−19.3 or −17.8)	−18.8	+0.5	−18.8	+1.0
Dinitromethane	−14.1	−14.4	+0.3	−13.6	−0.5
Trinitromethane	−3.2	−2.7	−0.5	−4.2	+1.0
Rxn 3					
Nitromethane	(−19.3 or −17.8)	−19.5	+0.2	−19.5	+1.5
Trinitromethane	−3.2	−0.9	−2.3	+0.6	−3.8
Methane	−17.89	−17.59	−0.30	−15.34	−2.55
Rxn 4					
Nitromethane	(−19.3 or −17.8)	−18.2	−1.1	−18.2	+0.4
Tetranitromethane	19.7	+15.3	+4.4	+21.3	−1.6
Methane	−17.89	−19.35	+1.46	−17.35	−0.54
Rxn 5					
Nitromethane	(−19.3 or −17.8)	−19.2	−0.1	−19.2	+1.4
Ethane	−20.04	−20.48	+0.44	−17.48	−2.56
Nitrous Acid	−18.34	−18.56	+0.22	−17.06	−1.28
Hydrogen (H_2)	0.0	+0.22	−0.22	−1.28	+1.28
Rxn 6					
Nitromethane	(−19.3 or −17.8)	−19.5	+0.2	−19.5	+1.7
1,1-Dinitroethane	−24.06	−23.67	−0.39	−20.67	−3.39
Hydrogen (H_2)	0.0	+0.43	−0.43	+3.43	−3.43
Rxn 7					
Nitromethane	(−19.3 or −17.8)	−18.7	−0.6	−18.7	+0.9
Methane	−17.89	−18.53	+0.6	−17.03	−0.9
Nitrous Acid	−18.34	−18.94	+0.6	−17.44	−0.9
Hydrogen (H_2)	0.0	+0.60	−0.6	−0.90	+0.9
Rxn 8					
Nitromethane	(−19.3 or −17.8)	−20.0	+0.7	−20.0	+2.2
Dinitromethane	−14.1	−12.42	−1.7	−9.42	−4.7
Propane	−25.02	−23.34	−1.7	−20.34	−4.7
Ethane	−20.04	−21.73	+1.7	−24.72	+4.7
Hydrogen	0.0	+1.69	−1.7	+4.69	−4.7

[a] Calculated heat of formation values for nitromethane were determined using the known experimental values for all of the other compounds in each isodesmic or hydrogenation reaction. For this reason, the calculated heat of formation values for nitromethane are *always identical* for each isodesmic or hydrogenation reaction examined. When the heat of formation values for each of the other components of the reactions were determined, known experimental values were used for these other components except the one whose heat of formation was being calculated. In these calculations, heat of formation values for *components other than nitromethane* were determined using *both* of the experimental heat of formation values that have been reported for nitromethane. When the −19.3 kcal/mol value was used a MAE of only 0.9 kcal/mol was calculated in contrast to a MAE of 2.2 kcal/mol calculated when the −17.8 kcal/mol value was used in these isodesmic and hydrogenation reactions.

Group additivity and the difference method

When a methylene group additivity value of −5.0 kcal/mol for each methylene group present is subtracted (i.e., using the difference method) from $\Delta_f H_g^0$ values estimated by the group additivity method for nitroethane, 1-nitropropane, and 1-nitrobutane, $\Delta_f H_g^0$ values of −19.4, −19.3, and −19.4 kcal/mole, respectively, are found for nitromethane (mean = −19.4 ± 0.1). When the same procedure is performed using experimentally determined data, values of −19.5, −19.7, and −19.3 kcal/mol, respectively, are found (mean = −19.5 ± 0.2 kcal/mol). A conventional group additivity approach can be taken if values of −9.3, −10.0, and −5.0 kcal/mol are used for the nitro group, methyl group, and methylene group, respectively. When this was done,

Table 3. Heat of formation values ($\Delta_f H_g^0$) (298k) in kcal/mol for several nitroalkanes calculated using density functional theory (B3LYP) and several basis sets coupled with the use of isodesmic and hydrogenation reactions (control rxns 1–6)

		Nitroethane	1-Nitropropane	1-Nitrobutane	2-Methyl-2-nitropropane	2-Methyl-2-nitropropane	1-Nitropropane
Method	Basis Set	Control Rxn 1	Control Rxn 2	Control Rxn 3	Control Rxn 4	Control Rxn 5	Control Rxn 6
B3LYP	6-31 G*	−27.2	−31.8	−37.7	−40.5	−43.7	−28.8
B3LYP	6-31 G**	−24.9	−30.3	−35.8	−40.7	−41.8	−29.0
B3LYP	6-31+G*	−27.0	−30.8	−36.4	−40.0	−41.6	−29.2
B3LYP	6-311 G*	−27.3	−31.8	−37.5	−40.8	−43.6	−29.0
B3LYP	6-311+G**	−24.1	−28.1	−33.8	−45.4	−44.4	−29.1
Mean ± SD	—	26.1 ± 1.5	−30.6 ± 1.5	36.2 ± 1.6	−41.5 ± 2.2	−43.0 ± 1.2	−29.0 ± 0.1
Exp't ± SD	—	−24.5 ± 0.2[a]	−29.6 ± 0.2[b]	−34.4 ± 0.5[c]	−42.32 ± 0.8[d]	−42.32 ± 0.8[d]	−29.6 ± 0.2[b]
MAE	—	1.76	1.56	2.1	2.1	1.0	0.8
PM3	—	—	—	—	−36.7	—	−29.4

[a] Experimental heat of formation for nitroethane.
[b] Experimental heat of formation for 1-nitropropane.
[c] Experimental heat of formation for 1-nitrobutane.
[d] Experimental heat of formation for 2-methyl-2-nitropropane.

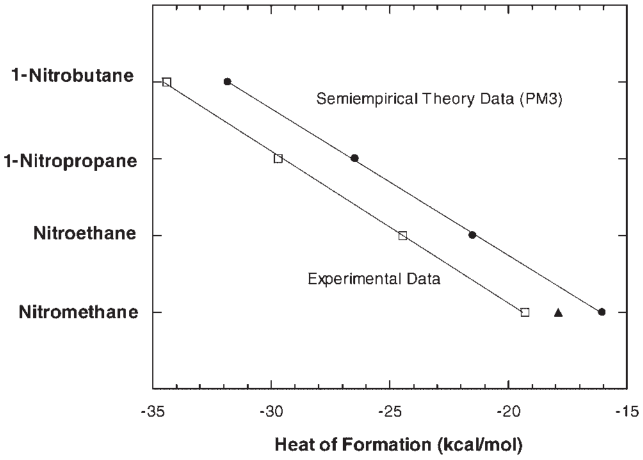


Figure 1. Heats of formation for nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane. Experimental results are compared with computed results calculated using the PM3 semiempirical model. Experimental results are represented by open squares. Because two experimental values have been reported for nitromethane, a closed triangle as well as an open square represent values for the experimental heats of formation reported for this compound. Computed results are represented by closed circles

$\Delta_f H_g^0$ values of −19.3, −24.3, −29.3, and −34.3 kcal/mol were calculated for nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane, respectively, and these values agree exceptionally well with experimental values to within a few tenths of a kcal/mol.

The relatively simple group additivity approaches used here support the lower experimental heat of formation. Nevertheless, these data should be viewed in light of the fact that the effect of group substitution on the $\Delta_f H_g^0$ of methyl derivatives is often somewhat different than it is for ethyl-, *n*-propyl-, and *n*-butyl-derivatives. For example, the absolute difference in the $\Delta_f H_g^0$ values of methanol and ethanol is 8.23 kcal/mol while the absolute differences in the $\Delta_f H_g^0$ values between ethanol and *n*-propanol and between *n*-propanol and *n*-butanol are more in keeping with the value of −5.0 kcal/mol for a methylene (—CH_2—) group (5.3 and 4.7 kcal/mol, respectively).

On the other hand, it is important to make the appropriate comparisons. Substituted methanes, compounds, such as acetic acid, acetaldehyde, acetonitrile, ethanol, ethanethiol, chloroethane, and acetamide, are among those compounds that are most comparable to nitromethane. Each can be viewed as a methane substituted with a carboxyl group, an aldehyde group, a nitrile group, a —CH_2OH group, a —CH_2SH group, a —CH_2Cl group, and an amide group, respectively, while nitromethane, of course, is a nitrosubstitued methane. When the difference method is used to calculate the $\Delta_f H_g^0$ of these compounds starting with the $\Delta_f H_g^0$ of higher homologs (such as 1-propanoic acid, propanal, propanenitrile, 1-propanol, 1-propanethiol, 1-chloropropane, propanamide, and nitroethane), $\Delta_f H_g^0$ values are calculated that closely agree with experimentally determined values, to within ±0.4 kcal/mol.

Weizmann-1 theory

W1 theory is among the most powerful and accurate multilevel *ab initio* computational theories available for use.[33–35] Given that an MAE of 0.3 kcal/mol has been demonstrated for $\Delta_f H_g^0$ values for some sets of test compounds, it was our original intent to use this level of theory as a definitive assessment in support of one of the experimental values for the $\Delta_f H_g^0$ of nitromethane that have been reported. At first glance, it would appear that the value of −18.1 kcal/mol that was computed, coupled with a reasonably small MAE, would support strongly the experimental value of −17.8 kcal/mol. However, we were not able to make this assessment with confidence. First of all, an appropriate MAE was required. To select an appropriate MAE, it seemed prudent to select the MAE value determined by Parthiban and Martin[35] in their study of the ability of W1 and W2 theory to accurately determine $\Delta_f H_g^0$ values of selected compounds in the G2-2 test set. For this set of 26 compounds, an MAE of 0.7 kcal/mol was determined. Furthermore, a maximum absolute error of 1.7 kcal/mol occurred in this test set and fully 14 of the 26 compounds tested in this set exhibited an absolute error of between 0.8 and 1.7 kcal/mol. When only those compounds containing a methyl group were considered, the MAE was calculated as 0.85. Also of concern is the fact that $\Delta_f H_g^0$ values for all four nitrogen oxides were overestimated. Thus, $\Delta_f H_g^0$ values for NO, NO_2, N_2O, and ClNO were overestimated by 0.7, 0.8, 0.8, and 1.6 kcal/mol, respectively. This leads us to question if the $\Delta_f H_g^0$ value for nitromethane and other NO_x compounds are also overestimated by a similar amount by this level of theory.

DFT/atomic equivalent approach

Mole *et al.*[36] developed a straightforward atom equivalent method that converts DFT energies to $\Delta_f H_g^0$ values. Using this method, they showed that the mean deviation between calculated and experimental $\Delta_f H_g^0$ values of 23 hydrocarbons was about ±2 kcal/mol. Rice *et al.*[22] expanded this procedure and showed that it could be used to accurately calculate the $\Delta_f H_g^0$ values of a variety of compounds containing nitro groups, including several high explosives. The $\Delta_f H_g^0$ for nitromethane was calculated to be -19.5 ± 0.2 kcal/mol.

DFT/atomization energy approach

Su *et al.*[37] used DFT with an atomization approach and several hybrid density functionals coupled with several basis sets to calculate the $\Delta_f H_g^0$ value of nitromethane. Results were rather scattered, ranging from −10.7 to −20.8 kcal/mol. These investigators compared their results to the experimental value of -19.3 ± 0.3 kcal/mol and noted that those $\Delta_f H_g^0$ values calculated with the B3LYP/6-31G**, the B3PW91/6-31G**, and the PBE0/6-31G** basis sets yield results most consistent with this experimental value. It turns out, however, that calculations performed using two other basis sets, B3PW91/6-31+G** and the PBE0/6-31+G**, yielded values more consistent with the higher experimental value.

Gaussian theory

As noted above, G1, G2, and G3 are highly accurate multilevel *ab initio* models[15–17] that have a semiempirical component and are parameterized to reproduce results from a set of test compounds and nitromethane is one of these test compounds. Thus, it is not altogether surprising that the most recent Gaussian model, G3, exactly reproduced the $\Delta_f H_g^0$ value of −17.8 kcal/mol for nitromethane as this value is a target value used in the development of this model.[17] Interestingly, a value of −20.5 kcal/mol was calculated by G2[18] theory while a value of −20.9 kcal/mol was calculated using G1 theory.[38]

Several modifications to G2 and G3 model chemistries have been developed.[18–21] Some of these modifications increase computational efficiency at the expense of a minor decrease in accuracy. For example, in the modification of G2 known as G2(MP2), a reduced order Møller–Plesset (MP2) calculation is substituted for the computationally expensive MP4 calculation.[18] Over the test set of 148 compounds, the average error is increased from 1.6 to 2.03 kcal/mol. In other modifications, different methods to acquire molecular geometries are used. In addition to Møller–Plesset perturbation theory, DFT was often used in the development of these modifications. Four modifications of G2 theory, G2(B3LYP), G2(B3PW91), G2(MP2), and G2(MP2,SVP) resulted in model chemistries that resulted in calculated $\Delta_f H_g^0$ values for nitromethane of −20.2, −22.8, −21.5, and −19.7 kcal/mol, respectively.[18] For G3 theory, four modifications, G3(MP3), G3(MP2), G3(B3LYP), and G3(MP2)//B3LYP, resulted in the calculation of $\Delta_f H_g^0$ values for nitromethane of −16.1, −16.2, −18.5, and −17.1 kcal/mol, respectively.[19,20] Although the range of these calculated values is from −16.1 to −22.8 kcal/mol for the $\Delta_f H_g^0$ of nitromethane, it should be appreciated that the average absolute deviation within any given model for the 148 compounds in the test set is typically very accurate, often between 0.9 and 2.0 kcal/mol. Exceptions to this include the G2 (B3LYP) and G2(B3PW91) models in which the average absolute deviations are 3.11 and 3.51 kcal/mol, respectively.[18]

Complete basis set model chemistry

The complete basis set (CBS) model chemistries developed by Peterson and associates[39–44] are also among the most rigorous and highly accurate multilevel *ab initio* computational models developed to date. ROCBS-QB3 and CBS-QB3 are reported to result in values having an MAE of 0.9 and 1.2 kcal/mol, respectively. For nitromethane, $\Delta_f H_g^0$ values of −19.0 and −19.6 kcal/mol were reported using the ROCBS-QB3 and CBS-QB3 model chemistries, respectively.[44]

Hartree–Fock/density functional theory calculation with a linear regression correction approach

Duan *et al.*[45] used a linear regression approach to account for electron correlation energy missing in Hartree–Fock *ab initio* calculations. Linear regression was also used to reduce inherent errors in calculating $\Delta_f H_g^0$ values using DFT. For Hartree–Fock calculations, this approach was useful for a variety of compounds, but not for most nitrogen-containing compounds. On the other hand, DFT coupled with a linear regression approach was effective for most of the 150 compounds tested. For DFT B3LYP 6-31 G(d), mean absolute deviation in the calculation of $\Delta_f H_g^0$ values of the 150 test compounds was reduced from 9.2 to 2.7 kcal/mol. For DFT B3LYP 6-311+G(d,p), mean absolute deviation for the calculation of $\Delta_f H_g^0$ values of the 150 test compounds was reduced from 18.2 to 2.4 kcal/mol. For the specific case of nitromethane, $\Delta_f H_g^0$ values of −20.6 and −19.3 kcal/mol were calculated using DFT B3LYP 6-31 G(d) and DFT B3LYP 6-311+G(d,p) basis sets, respectively. Interestingly, the authors used the experimental value of −17.9 kcal instead of the −19.3 kcal/mol experimental value for purposes of comparison.

Molecular mechanics (MM2 and MM3)

Molecular mechanics force fields (MM2 and MM3) have been developed that calculate well the $\Delta_f H_g^0$ values of several monosubstituted alkanes.[46] In development of these force fields, experimental values for nitroalkanes were taken from Pedley's *Thermochemical Data of Organic Compounds*[7] and these compounds were used in the development of these models. For nitromethane, the $\Delta_f H_g^0$ value was calculated to be −17.76 (= −17.8) kcal/mol. It is unclear what affect an assumed experimental $\Delta_f H_g^0$ value of −19.3 kcal/mol might have had on the development of these force fields as they pertain specifically to nitromethane.

Atomic equivalent approach for converting density functional energies calculated using molecular mechanics force field energies to heats of formation

Rousseau and Mathieu[47] developed an approach in which cost-effective heat of formation values can be calculated by combining DFT with a molecular mechanics force field. In this approach, atom equivalents converted DFT BPDN**//MMFF energies into $\Delta_f H^0_g$ values. Using procedures termed PIMM, P1, and P2, the authors calculated $\Delta_f H^0_g$ values for nitromethane of −23.2, −20.9, and −20.8 kcal/mol, respectively.

BAC-MP4 and BAC-G2 theory

Chemically based hybrid bond-additivity correction (BAC) approaches have been developed by Melius *et al.*[48–50] at several high levels of theory, including Gaussian 2 theory (BAC-G2) and Møller–Plesset perturbation theory at the MP4 level (BAC-MP4). BAC-G2 is regarded as being more accurate. Nitromethane $\Delta_f H^0_g$ values calculated by Dr Carl Melius using BAC-MP4 and BAC-G2 are -16.83 ± 1.59 and -18.76 ± 1.02, respectively (Personal communication from Dr Mark Allendorf).

Observations regarding experimental data

Given that the genesis of this discrepancy has its origins at the laboratory bench, it seems prudent to put *in silico* analysis aside for a moment and examine in some detail the experimental research that resulted in these two $\Delta_f H^0_g$ values for nitromethane. It turns out that the thermochemistry of nitromethane has been studied for well over 100 years (Table 4).

To determine the gas phase heat of formation ($\Delta_f H^0_g$), the heat of combustion ($\Delta_c H^0_{\text{liquid}}$) is first determined by calorimetery. Once a value for $\Delta_c H^0_{\text{liquid}}$ is in hand, the liquid phase heat of formation ($\Delta_f H^0_{\text{liquid}}$) for nitromethane is calculated using the following:

$$\Delta_c H^0_{\text{liquid}} = [\Delta_f H^0_g(\text{CO}_2) + 1.5\Delta_f H^0_{\text{liquid}}(\text{H}_2\text{O}) + 0.5\Delta_f H^0_g(\text{N}_2)] - [\Delta_f H^0_g(\text{CH}_3\text{NO}_2) + 0.75\Delta_f H^0_g(\text{O}_2)]$$

where:

$$\Delta_f H^0_g(\text{CO}_2) = -94.051 \pm 0.031\ \text{kcal/mol}$$
$$\Delta_f H^0_{\text{liquid}}(\text{H}_2\text{O}) = -68.3150 \pm 0.0096\ \text{kcal/mol}$$
$$\Delta_f H^0_g(\text{O}_2) = 0\ \text{kcal/mol}$$
$$\Delta_f H^0_g(\text{N}_2) = 0\ \text{kcal/mol}$$

Finally, the gas phase heat of formation is calculated by adding the heat of vaporization ($\Delta_{\text{vap}} H^0$) to $\Delta_f H^0_{\text{liquid}}$.

$$\Delta_f H^0_g = \Delta_f H^0_{\text{liquid}} + \Delta_{\text{vap}} H^0$$

Values of 8.24 ± 0.02, 9.168, 9.09 ± 0.09, and 9.171 kcal/mol have been reported for the $\Delta_{\text{vap}} H^0$ of nitromethane.[6] The $\Delta_{\text{vap}} H^0$ value of 9.171 kcal/mol appears to be the one most widely used. For consistency, this value for the $\Delta_{\text{vap}} H^0$ of nitromethane was used in these calculations. In Table 4, the original $\Delta_c H^0_{\text{liquid}}$ values reported in eight studies[5,8,51–56] published since 1886 are presented. From these original $\Delta_c H^0_{\text{liquid}}$ values, $\Delta_f H^0_{\text{liquid}}$ and finally $\Delta_f H^0_g$ values were calculated as described above and are also presented in Table 4.

It appears that the three highest $\Delta_f H^0_g$ values (−15.65 and −12.10 and −12.95 kcal/mol) are too high and are incorrect. This leaves four studies[8,51,53,54] reporting $\Delta_f H^0_g$ values between −17.55 and −17.95 kcal/mol and one reporting a value of −19.35 kcal/mol.[5] Unfortunately, the procedures for the experimental $\Delta_f H^0_g$ values reported by McCullough *et al.*[8] were not presented in their manuscript as this value was based on a personal communication to the authors from Edward J. Prosen, an experienced chemist at the National Bureau of Standards (Washington, DC). Similarly the procedures used by Lebedeva and Ryadnenko[51] were not well described. Their procedures noted only that the purity of the nitroalkanes analyzed was 99.9% or greater and that the heats of combustion were determined at 25°C in a calorimeter having a thermal jacket. In contrast, the study by Knobel *et al.*,[5] who reported a $\Delta_f H^0_g$ value of

Table 4. Thermochemical values (298k) reported for nitromethane since 1886[a]

	$\Delta_c H^0_{\text{liquid}}$ (kcal/mol)	$\Delta_f H^0_{\text{liquid}}$ (kcal/mol)	$\Delta_f H^0_g$ (kcal/mol)	Author(s), year published, and references
1	−171.7	−24.82	−15.65	Thomsen (1886)[52]
2	−169.4	−27.12	−17.95	Berthelot and Matignon (1893)[53]
3	−169.8	−26.72	−17.55	Swientoslawski (1910)[54]
4	-175.25 ± 0.18	−21.27	−12.10	Holcomb and Dorsey (1949)[55]
5	[b]	−27.03	−17.86	McCullough *et al.* (1954)[8]
6	-174.4 ± 0.3	−22.12	−12.95	Cass *et al.* (1958)[56]
7	-168.0 ± 0.3	−28.52	−19.35	Knobel *et al.* (1971)[5]
8	-169.6 ± 0.1	−26.92	−17.75	Lebedeva and Ryadnenko (1973)[51]

[a] Except for the study of McCullough *et al.*,[8] the initial thermochemical value reported was the $\Delta_c H^0_{\text{liquid}}$ which was then converted to $\Delta_f H^0_{\text{liquid}}$ and then to $\Delta_f H^0_g$ as described in the text.

[b] The value for $\Delta_f H^0_{\text{liquid}}$ was received by the authors[8] as a personal communication and converted to $\Delta_f H^0_g$ as described in the text.

Table 5. Summary of nitromethane heat of formation values ($\Delta_f H^0_g$) (298k) in kcal/mol determined by experiment or calculation

Method	Level of theory or method abbreviation	$\Delta_f H^0_g$ kcal/mol	Uncertainty[a] kcal/mol	Author(s), year, and references
DFT linear regression	B3LYP 6-31 G(d)	-20.6	2.7	Duan *et al.* 2004[45]
DFT linear regression	B3LYP 6-311+G(d,p)	-19.3	2.4	Duan *et al.* 2004[45]
Complete basis set	ROCBS-QB3	-19.0^{b}	0.9 ± 0.4^{b}	Wood *et al.* 2006[44]
Complete basis set	CBS-QB3	-19.6^{b}	1.2 ± 0.4^{b}	Wood *et al.* 2006[44]
DFT/atomization	B3LYP/6-31 G**	-18.7	—	Su *et al.* (2007)[37]
DFT/atomization	B3PW91/6-31G**	-20.3	—	Su *et al.* (2007)[37]
DFT/atomization	PBE 0/6-31G**	-20.8	—	Su *et al.* (2007)[37]
DFT/atomization	B3PW91/6-31+G**	-16.9	—	Su *et al.* (2007)[37]
DFT/atomization	PBE0/6-31+G**	-17.4	—	Su *et al.* (2007)[37]
DFT/atomic equivalent	B3LYP/6-31 G*	-19.5	±0.2	Rice *et al.* (1999)[22]
Gaussian	G1	-20.9	2.0	Dorsett and White (2000)[38]
Gaussian	G2	-20.5	1.2	Curtiss *et al.* (1997)[18]
Gaussian	G3	-17.8	1.1	Curtiss *et al.* (1998)[17]
Gaussian	G2(B3LYP)	-20.2	3.11	Curtiss *et al.* (1997)[18]
Gaussian	G2(B3PW91)	-22.8	3.51	Curtiss *et al.* (1997)[18]
Gaussian	G2(MP2)	-21.5	2.03	Curtiss *et al.* (1997)[18]
Gaussian	G2(MP2, SVP)	-19.7	1.93	Curtiss *et al.* (1997)[18]
Gaussian	G3(MP3)	-16.1	1.2	Baboul *et al.* (1999)[20]
Gaussian	G3(MP2)	-16.2	1.18	Curtiss *et al.* (1999)[19]
Gaussian	G3(B3LYP)	-18.5	0.96	Baboul *et al.* (1999)[20]
Gaussian	G3(MP2)//B3LYP	-17.1	1.13	Baboul *et al.* (1999)[20]
Weizmann	W1	-18.1	±0.7 to ±1.0	This study
DFT	B3LYP/6-31 G*	-19.7	±1.0	This study
DFT	B3LYP/6-31 G**	-19.2	±0.6	This study
DFT	B3LYP/6-31+G*	-20.7	±1.1	This study
DFT	B3LYP/6-311 G*	-19.8	±0.9	This study
DFT	B3LYP/6-311+G**	-19.9	±1.7	This study
Semiempirical	PM3	-20.0^{c}	$\pm 1.6^{c}$	This study
Group additivity	Direct Calculation	-19.3	$\pm 0.6^{d}$	This study
Group additivity	Difference method	-19.4	$\pm 0.1^{e}$	This study
Group additivity	Difference method	-19.5	$\pm 0.2^{f}$	This study
MP4 hybrid, bond-additivity correction	BAC-MP4	-16.83	±1.59	Allendorf, personal communication
Gaussian 2 hybrid, bond-additivity correction	BAC-G2	-18.76	±1.02	Allendorf, personal communication
DFT BPDN**//MMFF	PIMM	-23.2^{b}	—	Rousseau and Mathieu (2000)[47]
DFT BPDN**//MMFF	P1	-20.9^{b}	—	Rousseau and Mathieu (2000)[47]
DFT BPDN**//MMFF	P2	-20.8^{b}	—	Rousseau and Mathieu (2000)[47]
Molecular mechanics	MM2	-17.76		Allinger *et al.* (1990)[46]
Molecular mechanics	MM3	-17.76		Allinger *et al.* (1990)[46]
Experiment	—	-19.3	±0.3	Knobel *et al.* (1971)[g] [5]
Experiment	—	-17.86	±0.1	McCullough *et al.* (1954)[h] [8]

[a] Uncertainty values are those reported by the authors, typically as mean absolute error (MAE) or mean ± SD. Refer to text for details.

[b] Originally reported in kJ/mol.

[c] Based on the use of isodesmic Rxns 1 to 3. Refer to text for details.

[d] This uncertainty value represents the fact that in Benson *et al.*[29] the $\Delta_f H^0_g$ of six nitroalkanes were predicted to within ±0.6 kcal/mol of the experimental values.

[e] Mean ± SD for nitromethane $\Delta_f H^0_g$ values obtained when a group additivity value of −5.0 kcal/mol for each methylene ($-CH_2-$) group was subtracted from group additivity $\Delta_f H^0_g$ values for nitroethane, 1-nitropropane, and 1-nitrobutane.

[f] Mean ± SD for nitromethane $\Delta_f H^0_g$ values obtained when a group additivity value of −5.0 kcal/mol for each methylene ($-CH_2-$) group was subtracted from experimental $\Delta_f H^0_g$ values for nitroethane, 1-nitropropane, and 1-nitrobutane.

[g] Value listed in NIST WebBook.[6]

[h] Value listed in *Thermochemical Data of Organic Compounds*.[7]

−19.35 kcal/mol, provides much more information regarding experimental detail. It was noted that nitromethane was dried under a vacuum over P_2O_5 and further purified via fractional distillation and still further purified by crystallization. After crystallization (50% yield), the purity of the sample used for combustion was reported to be 99.87%. The use of standards to determine the thermal value of the semi-microcalorimeter was noted. The Washburn correction was also used. The Washburn correction accounts and controls for several phenomena that occur during calorimetric determinations, including weight loss due to vaporization and the non-isothermicity of the combustion process.[57] The heat of combustion value was reported as the mean ± SD of 10 replicates. In 3 of the 10 replicates, carbon dioxide recovery was determined. In these controls, it was shown that 99.87, 99.61, and 99.98% of the theoretical carbon dioxide formed during combustion was recovered. It is also worth noting that Knobel *et al*.[5] were well aware of the results of several earlier workers and that it was their obvious intention to provide more reliable data. We have not examined the original papers of Berthelot and Matignon[53] and of Swientoslawski,[54] published in 1893 and 1910, respectively. However, it is safe to say that the Washburn correction was not used in these early investigations as this correction factor was not developed until the 1930s.

To summarize the experimental data, it appears to us that the small differences in heat of combustion values (the initial thermodynamic values needed to determine heats of formation) are likely due to the slightly different ways in which careful investigators used necessary correction factors (such as the Washburn correction) and other controls to analyze calorimetric data.

Recommendation

At this juncture, it is necessary to provide a recommendation regarding which experimental value is best supported by the computational data. Data from all of the computational models examined or reviewed are summarized in Table 5. Of the theoretical models that have been used to determine $\Delta_f H_g^0$ values of nitromethane, Peterson's CBS models[39–44] and Weizmann W1[33–35] are both well characterized, exceptionally rigorous and able to provide accuracies approaching chemical accuracy of ~1.0 kcal/mol. ROCBS-QB3 and CBS-QB3 are reported to have MAEs of 0.9 and 1.2 kcal/mol, respectively and W1 has a reported MAE of 0.7 kcal/mol for molecules about the size of nitromethane in the G2-2 test set. Unfortunately, the CBS models best support the −19.3 kcal/mol value whereas the W1 value of −18.1 ± 0.7 kcal/mol is closer to the −17.8 kcal/mol value. It was surprising that two of the most rigorous and very accurate models evaluated for this investigation did not exhibit results that were more mutually supportive in this particular case. This leaves us to examine the other computational models that have addressed this problem. Thus, DFT linear regression analysis[45] and the DFT atomic equivalent approach[22] both support the −19.3 kcal/mol value as the does the group additivity approach and the semiempirical PM3 model experiments that we describe. Some of the Gaussian model chemistries, G2 and G3 and their several modifications are also able to provide accuracies that approach chemical accuracy. G2 and its modifications support the lower $\Delta_f H_g^0$ value for nitromethane while G3 and its modifications are more supportive of the higher value. Interestingly, two Gaussian models G3(B3LYP) and BAC-G2 provide $\Delta_f H_g^0$ values that are intermediate between the two experimental values.

Finally, we are left to examine the DFT experiments presented here. Average heats of formation determined using DFT coupled with the use of four isodesmic reactions and four hydrogenation reactions using five different basis sets all cluster nearer the −19.3 kcal/mol value (Table 1). Also important is the fact that the −19.3 kcal/mol value is more accurate compared to the −17.8 kcal/mol value when used to calculate heats of formation of other nitroalkanes using these same isodesmic and hydrogenation reactions (Table 2).

Thus, it is recommend that the experimental value of −19.3 kcal/mol be used for investigations requiring a heat of formation for nitromethane. This recommendation is based on the observation that CBS model chemistries, G2 model chemistries, the DFT linear regression approach, the DFT atomization approach, the semiempirical (PM3) approach, group additivity results, DFT studies coupled with the use of isodesmic and hydrogenation reactions all support this value.

Summary

Of the *experimental* $\Delta_f H_g^0$ values that have been published for nitromethane, data presented here coupled with an exhaustive examination of experimental and computational data in the literature currently best support the value of −19.3 ± 0.3 kcal/mol that is reported by Knobel *et al*.[5] and listed in the NIST WebBook.[6] Previously published results dependent on the use of the value of McCullough *et al*.[8] listed in Pedley's *Thermochemical Data of Organic Compounds*[7] should be reevaluated using the lower value and further development of semiempirical methods should consider using this value in future reparameterization efforts.

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