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The thermochemistry of TNAZ (1,3,3-trinitroazetidine) and related species: G3(MP2)//B3LYP heats of formation

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Abstract

The heats of formation of TNAZ(1,3,3-trinitroazetidine) and related compounds have been calculated with the G3(MP2)//B3LYP model to give a mean absolute error of 0.85 kcal/mol for 16 singlet species and 0.61 kcal/mol for 12 free radical intermediates. These uncorrected errors are better than our previous B3LYP/6-31G(d,p)-based scheme that employed *seven* auxiliary parameters. The mean absolute deviation of the G3(MP2)//B3LYP energies of the combined set of 28 singlet and radical species, 0.75 kcal/mol, can be reduced to 0.42 kcal/mol when supplemented with a minimal *four*-parameter atom-based correction scheme. It was found that the previous B3LYP/6-31G(d,p) energies when fitted to a combination of 39 experimental and G3(MP2)//B3LYP singlet and radical species gave a mean absolute deviation of 3.7 kcal/mol, but that the error is reduced to 1.52 kcal/mol when the B3LYP/6-31G(d,p) energies are supplemented with a *five* parameter additive correction scheme. The results of these calculations are used to clarify the initial mechanistic steps in the decomposition of TNAZ. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Density functional theory; B3LYP; G3(MP2)B3LYP; Thermochemistry; TNAZ

1. Introduction

As part of our study [1] of the gas phase pyrolysis of TNAZ (1,3,3-trinitroazetidine), a member of the “new generation” explosives, we developed a computational model that could be used to predict the energies of both the singlet and radical species involved in their decompositions and to offer insights into the structural basis for those energies. The approach taken [2] was to perform DFT B3LYP/6-31G(d,p) calculations, and to supplement them with an empirical seven parameter scheme that reduced the mean absolute deviations [MAD] for the singlets from 3.1 to 1.1 kcal/mol

and for the radicals from 5.1 kcal/mol) to 1.3 kcal/mol, respectively.

Based on these calculations a set of structural enthalpy increments was compiled that allowed a precise estimation of heats of formation of highly nitrated species from simpler ones via isodesmic reactions that are independent of atom/group additivity parameters. In a parallel analysis, an augmented Benson group-additivity scheme was developed that allowed facile estimation of the heats of formation of the several nitroazetidines, as well as related radical species, with a precision that is comparable to that obtained via quantum mechanical calculations.

In this paper, we have recalculated the energies of most of these species using the new G3(MP2)//B3LYP method [3], which on the demanding G2/97 test set of 299 energies produces an average absolute

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Table 1

Calculated G3(MP2)//B3LYP/6-31G(d) singlet enthalpies (298.15 K) with and without empirical corrections

Compound	Calc. enthalpy ^a (298.15 K)	ΔH_f^{0b} (Calc.)	ΔH_f^{0b} (Adjusted)	ΔH_f^{0b} (Obs.)	S ⁰ (eu)
Methane	−40.420557	−17.52	−18.08	−17.78	47.2
Ethane	−79.651022	−19.68	−20.19	−20.03	54.4
Propane	−118.885804	−24.55	−25.01	−25.02	64.1
Cyclobutane	−156.896600	7.20	7.40	6.79	65.7
Ammonia	−56.469220	−10.14	−11.50	−10.98	46.0
Methyl amine	−95.686725	−4.17	−5.49	−5.50	57.3
Dimethyl amine	−134.911783	−2.94	−4.21	−4.45	64.7
Ethyl amine	−134.924319	−10.81	−12.07	−11.33	64.7
Nitromethane	−244.710392	−16.76	−17.67	−17.76	70.1
Dinitromethane	−448.989461	−9.26	−10.50	−14.08 ^c	85.2
Nitroethane	−283.948849	−23.94	−24.80	−24.45	74.9
1-Nitropropane	−323.183321	−28.62	−29.43	−29.59	85.3
2-Nitropropane	−323.189776	−32.67	−33.48	−33.22	81.5
2,2-Dinitropropane	−527.480883	−32.72	−33.86	−28.84 ^{c,d}	93.2
Nitrobenzene	−436.133790	14.11	15.90	16.13	81.8
Nitroamine	−260.739315	3.00	1.29	0.57 ^c	64.1
N-nitrodimethylamine	−339.197475	0.41	−1.20	−1.15	80.3
Azetidine	−172.928901	24.84	24.24	23.47	65.1
N-Nitroazetidine	−377.219238	25.28	24.33		78.7
3-Nitroazetidine	−377.228309	19.59	18.64		81.1
1,3-Dinitroazetidine	−581.51324	23.42	22.13		94.3
1,3,3-Trinitroazetidine	−785.79785	27.58	26.22		108.1
	MAD	0.85 (0.75) ^f	0.32 (0.42) ^f	N = 16	
	RMS	0.86 (0.89) ^f	0.42 (0.71) ^f		

^a In hartrees.^b In kcal/mol.^c Not included in averages or in determining correction parameters.^d Estimated from the ΔH_f^0 of liquid combined with the heat of vaporization of 1,1-dinitropropane.^e Average of G3 and CBS-QB3 calculations (see text).^f Statistic based on combined set of 28 singlets and radicals from Tables 1 and 2.

error of only 1.25 kcal/mol. The new results provide a test of our earlier approach and serve as the basis for a new empirical correction scheme that reduces the misfit to only 0.47 kcal/mol on the set of 23 species related to TNAZ. Of major significance, the new results indicate that three of the generally quoted experimental heats of formation for species considered here are probably in error by more than 4 kcal/mol, and for these species still higher level G3 calculations are presented (which confirm the experimental discrepancies).

2. Computational model

All of the DFT and ab initio results reported in this

paper were calculated using G98W [4]. The principal computational model employed was the new G3(MP2)//B3LYP model developed by Baboul et al. [3]. This model, a simplified version of the full G3 model [MAD = 1.0 kcal/mol], runs about 7 × faster than G3, but still produces excellent results [MAD = 1.25 kcal/mol] with the G2/97 test suite of 299 energies.

For several of the species presented here no experimental data are available, and for the smaller of these we have calculated their energies by both the full G3 model and its computational competitor, Petersson's CBS-QB3 model [MAD = 1.0 kcal/mol]. Several other species were too large to allow G3 or CBS-QB3 calculations to be performed with our available resources. For these we can report only the G3(MP2)//

Table 2

Calculated G3(MP2)//B3LYP/6-31G(d) radical enthalpies (298.15 K) with and without empirical corrections

Compound	Calc. enthalpy ^a (298.15hK)	ΔH_f^{0b} (Calc.)	ΔH_f^{0b} (Adjusted)	ΔH_f^{0b} (Obs.)	S ⁰ (eu)
Hydrogen	−0.49791	52.10	51.80	52.10	27.4
Nitro	−204.86021	8.56	7.91	7.91	57.4
Methyl	−39.75476	34.56	34.30	35.10	50.2
Ethyl	−78.99052	29.07	28.87	28.40	61.1
1-Propyl	−118.37717	25.00	24.85	23.90	69.4
2-Propyl	−118.38347	21.86	21.70	22.00	70.0
Cyclobutyl	−156.44490	55.10	55.61	51.14 ^c	69.8
Amino	−55.85081	44.17	43.12	45.50	46.5
Methylamino	−95.13741	42.94	41.93	43.17 ^d	58.5
Dimethylamino	−134.42710	38.75	37.79	38.70 ^d	69.3
Nitromethyl	−244.29972	32.35	31.75	30.40	67.0
2-Nitro-2-propyl	−322.89431	9.18	8.68		84.3
Azetidin- <i>N</i> -yl	−172.49566	66.58	66.28	66.96	67.4
Azetidin-3-yl	−172.47792	74.05	73.75	74.55	67.3
3-Nitroazetidin- <i>N</i> -yl	−376.98809	61.05	60.40		83.2
3-Nitroazetidin-3-yl	−376.96880	65.07	64.43		80.3
<i>N</i> -Nitroazetidin-3-yl	−376.98181		75.42	74.78	82.7
3,3-Dinitroazetidin- <i>N</i> -yl	−581.46665	64.03	63.05		98.3
3-Nitro- <i>N</i> -nitroazetidin-3-yl	−581.46475	71.33	70.35		95.8
	MAD	0.61 (0.75) ^e	0.58 (0.42) ^e	N = 12	
	RMS	0.87 (0.89) ^e	0.94 (0.71) ^e		

^a In hartrees.^b In kcal/mol.^c Not included in averages or in determining correction parameters.^d Average of G3 and CBS-QB3 calculations (see text).^e Statistic based on combined set of 28 singlets and radicals from Tables 1 and 2.

B3LYP results. In total 22 singlet species and 19 radical species were considered, for roughly half of which experimental heats of formation have been published. The results are assembled in Tables 1 and 2.

In our previous report [2], the MAD of the B3LYP/6-31G(d,p) fit could be sharply reduced by a seven-parameter empirical scheme. The present G3(MP2)/B3LYP results achieve a slightly better fit directly. However, to ascertain whether the fit could be improved, we developed a *four*-parameter atom-additivity scheme; the parameters were evaluated using the add-in “Solver” optimization tool in the Excel spreadsheet program.

We updated our earlier B3LYP/6-31G(d,p) + seven-parameter correction scheme by fitting the experimental heats of formation combined with G3(MP2)/B3LYP heats for missing species. We found that a simpler five-parameter scheme worked acceptably well.

3. Calculated and corrected G3MP2B3 enthalpies

The 22 entries in column 3 of Table 1 (singlet species) and the 19 entries in column 3 of Table 2 (radical species) are the calculated reference enthalpies of formation (at 298 K); these include scaled zero-point and thermal energies. The heats of formation at 298.15 K were obtained using the corresponding calculated enthalpies for the atoms H, C, N and O and the experimental standard heats of formation of these atoms. The experimental gas-phase enthalpies in column 5 of Tables 1 and 2 were taken from the Pedley et al. collection [5] or the NIST data bank [6], unless otherwise noted in the footnotes to the tables. The four exceptions are the ΔH_f^0 of: nitroamine, NH_2NO_2 ; cyclobutyl radical; C_4H_7 , methylamino radical, CH_4N ; and dimethylamino radical, $\text{C}_2\text{H}_6\text{N}$. These were each assigned as the average of the calculated ΔH_f^0 using (a) the “high accuracy” G3

Table 3

Reference G3 and CBS-QB3 enthalpies (kcal/mol at 298.15 K) of selected species

Species	ΔH_f^0 , G3	ΔH_f^0 , CBS-QB3
Nitroamine	2.16	−1.02
Cyclobutyl radical	55.65	56.11
Methylamino radical	43.11	43.21
Dimethylamino radical	38.80	38.67

method of Pople et al. [7] and (b) the CBS-QB3 method of Petersson et al. [8]. Each of these models when applied to the standard G2/97 set of 299 energies results in a mean absolute deviation from experiment of 1.0 kcal/mol, and the average is probably as reliable as several of the experimental values used in the present study. These calculated ΔH_f^0 are collected in Table 3. The G3 and CBS-QB3 results for the two radicals agree well, but those for nitroamine differ considerably. To avoid an overly optimistic fit of the data, these three data points were excluded from the least squares analysis. Also excluded from the analysis were the data points for dinitromethane, 2,2-dinitropropane, and the cyclobutyl radical because they fall four or more standard deviations from the least-squares line. Exclusion of these three points can be rationalized as follows: dinitromethane is an explosive for which it is difficult to measure its heat of combustion. 2,2-Dinitropropane is a solid and its heat of vaporization is only an estimated value; it may also have combustion problems. The cyclobutyl radical ΔH_f^0 is based on a kinetic activation energy, which is possibly convoluted with a cyclopropylcarbinyl rearrangement [8]. The G3 and CBS-QB3 ΔH_f^0 agreed closely (see Table 3) with the G3(MP2)//B3LYP model.

Although the G3(MP2)//B3LYP model gave excellent results, it was of interest to determine if they could be improved by inclusion of empirical additive atomic corrections. The formulation tested was

$$\Delta H_f^0(\text{corrected}) = \Delta H_f^0(\text{calculated}) + n_H^*P(H) + n_C^*P(C) + n_N^*P(N) + n_O^*P(O)$$

where n_H is the number of H atoms in the molecule and $P(H)$ is the corresponding empirical constant, etc. The parameters were adjusted so

Table 4

Empirical parameters to correct the calculated G3MP2B3LYP energies

Parameter	Value (kcal/mol)	Parameter	Value (kcal/mol)
P(H)	−0.323	P(C)	0.717
P(N)	−0.225	P(O)	−0.221

as to minimize the mean absolute deviations between the adjusted values and the available experimental heats of formation (23 singlet and radical species). The values (in kcal/mol) found for these parameters are given in Table 4; they lead to a MAD value of only 0.42 kcal/mol. This precision is superior to that found with the computationally more expensive G3 and CBS-QB3 models. It is not clear how much of this improved fit is due to corrections of model deficiencies and how much results from fitting the experimental noise of a limited data set. A weak test comes from expanding the data set to include the four species in Table 3 for which only a high-level calculation of the ΔH_f^0 is available. When this is done the MAD value actually drops to 0.40 kcal/mol (with or without reoptimization of the parameters), which, if nothing else, demonstrates a high degree of internal consistency. Nonetheless, extrapolation to different data sets should not be undertaken without additional calibration; small variations in the experimental data or inclusion of new compounds could produce large changes in the individual parameters.

With respect to the values of the parameters, two points are worth making. First, the increment for a CH_2 group is very small ($0.717 - 2 \times 0.323 = 0.071$ kcal/mol), which means that the effect of including the parameters falls largely on the amines and nitro compounds. Indeed, the largest deviations occur with the amino and nitromethyl radicals. The second point is that the G3 family of methods include large empirical “higher level corrections” that are proportional to the difference in the number of α and the number of β electrons found in an isolated atom and those in the molecule formed from the atoms. For example, the ΔH_f^0 of a singlet molecule calculated by G3(MP2)//B3LYP contains an empirical correction of 6.12 kcal/mol for each C atom present. Against this backdrop the empirical adjustments proposed here are fairly small.

Table 5

Empirical parameters to estimate G3MP2B3LYP enthalpies from B3LYP enthalpies

Parameter	Value (kcal/mol)	Parameter	Value (kcal/mol)
Q(C)	−1.434	Q(H)	1.120
Q(N)	0.557	Q(O)	−0.258
Q(C-rad)	3.009	Q(N-rad)	2.870

4. Comparison of G3(MP2)//B3LYP enthalpies with those obtained from B3LYP calculations

G3(MP2)//B3LYP calculations consume a fair amount of computer resources; the two slow steps of the 1,3,3-trinitroazetidine calculation required 27 days on a 500 MHz PC. It clearly was of practical interest to see if the G3(MP2)//B3LYP energies could be estimated from the much faster running B3LYP/6-31G(d,p) calculations reported earlier.

To this end we set up an empirical additive atomic correction scheme similar to that employed above, but augmented by two additional parameters for the number of carbon and nitrogen radical sites present. Specifically, the formulation tested was

$$\begin{aligned}\Delta H_f^0(\text{est. G3MP2B3}) = & \Delta H_f^0(\text{B3LYP}) + n_H^* Q(\text{H}) \\ & + n_C^* Q(\text{C}) + n_N^* Q(\text{N}) \\ & + n_O^* Q(\text{O}) + n_{\text{C-rad}}^* Q(\text{C} \\ & - \text{rad}) + n_{\text{N-rad}}^* Q(\text{N} - \text{rad}).\end{aligned}$$

The parameters obtained by minimizing the absolute deviations between the estimated and exact G3(MP2)//B3LYP results for the combined set of 37 singlet and radical species are listed in Table 5. The MAD value for this set was 1.40 kcal/mol. This means that G3(MP2)//B3LYP values are readily estimated

with a precision that is not much larger than the MAD value for the comparison of G3(MP2)//B3LYP values with experimental values. The derived G3(MP2)//B3LYP values could then be used to estimate experimental values.

This high quality fit and the linearity of the fitting model implies that the B3LYP values also could be used to estimate “experimental” values directly. A simple five-parameter empirical additive atomic correction scheme was explored:

$$\begin{aligned}\Delta H_f^0(\text{expt}) = & \Delta H_f^0(\text{B3LYP}) + n_H^* R(\text{H}) + n_C^* R(\text{C}) \\ & + n_N^* R(\text{N}) + n_O^* R(\text{O}) \\ & + (n_{\text{C-rad}} + n_{\text{N-rad}})^* R(\text{rad}).\end{aligned}$$

In this scheme, unlike our previous publication, no distinction is made between radicals centered on carbon and nitrogen (inclusion of such a distinction lowers the MAD by a trivial 0.01 kcal/mol). The parameters were obtained by minimizing the absolute deviations between the corrected B3LYP enthalpies and the combined set of experimental heats of formation, G3 and/or CBSQ enthalpies, [and where no other data were available G3(MP2)//B3LYP enthalpies] a total set of 39 singlet and radical species. These derived parameters are listed in Table 6; the MAD value for this set was 1.51 kcal/mol. This is not quite as good a fit as experiment vs. G3(MP2)//B3LYP calculations, but considering that we are operating near the limit of practical G3(MP2)//B3LYP calculations, this empirical B3LYP fit provides a useful computational tool.

Because of the possible confusion from having three sets of parameters for computational models of similar names, it should be emphasized that the parametric corrections of the G3(MP2)//B3LYP energies are quite small and could be artifacts from the choice of the 28 reference compounds. The much larger parametric corrections of the B3LYP/6-31G(d,p) energies are largely associated with the N- and C-radical species. The parameters obtained by fitting the singlet species separately do not change drastically, which indicates that there is a genuine problem with the B3LYP treatment of N and C radicals.

Table 6

Empirical parameters to estimate experimental enthalpies from B3LYP enthalpies

Parameter	Value (kcal/mol)	Parameter	Value (kcal/mol)
R(C)	−0.603	R(H)	0.676
R(N)	0.492	R(O)	−0.597
R(rad)	3.612		

5. Mechanistic implications of the G3MP2B3 enthalpies for TNAZ decomposition

The thermal decomposition of TNAZ in the solid phase has been followed by IR analysis of the products [9]. It has also been studied by photofragmentation translational spectroscopy of a low-pressure molecular beam [10]. The time evolution has been tentatively interpreted as a competitive loss of NO₂ from N and C-3 with comparable activation enthalpies [10]. In our previous report describing the B3LYP//6-31G(d,p) calculations [2], the heats of formation of the two immediate products, 3,3-dinitroazetidin-*N*-yl radical and *N*,3-dinitroazetidin-3-yl radical were quite similar ($\Delta\Delta H_f^0 = 0.5$ kcal/mol). However, as noted above, these enthalpies were derived with quite large uncertainties. When the seven-parameter model developed in the earlier paper was applied to these radicals, the ($\Delta\Delta H_f^0$) increased to 2.6 kcal/mol favoring loss of the *N*-nitro. The present G3(MP2)//B3LYP calculations without corrections indicate that *N*-nitro loss is favored by 8.2 kcal/mol. This large gap, which is well beyond the uncertainty of the calculations, does not change when the empirical corrections are added because the two radicals are isomers and all atom-additive corrections cancel. The inescapable conclusion is that in the gas phase an initial loss of *N*-nitro from TNAZ is *strongly* favored.

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