Combined Molecular Orbital and Group Additivity Approach for Modeling Thermochemical Properties: Application to Hydrazides

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Heats of formation are often unavailable for compounds involved in synthesis, scale–up, or modeling of commercial products. This is true for agrochemicals developed at Rohm and Haas which are derived from hydrazides. I have computed heats of formation for five substituted hydrazides using AM1, HF/6-31G*, MP2/6-311G**, and MP4/6-311G**. The computed heats of formation were also used to derive a missing Benson group additivity equivalent for hydrazide. This equivalent makes it possible to compute heats of formation for hydrazides very easily using group additivity. Molecular orbital calculations are likely to be a valuable source for thermochemical information in the future, and this work shows their utility for extending group additivity into new classes of compounds previously inaccessible due to lack of experimental thermochemical data.

INTRODUCTION

Thermochemistry plays a crucial role in all chemical reactions, including many industrial applications such as synthesis, process development, and catalysis. Predicting gas-phase heats of reaction is simple if enthalpies of formation are available for all reactants and products. Unfortunately, often they are not. Where experimentally unavailable, heats of formation can sometimes be computed using a variety of methods such as group additivity[1–3] or molecular orbital (MO) calculations.[4–13] The group additivity method pioneered by Benson[1] and extended by Pedly, Naylor, and Kirby[2] is a powerful tool for determining heats of formation. This approach is simple and remarkably accurate, often predicting heats of formation within 1–2 kcal/mol. The most serious shortcoming of group additivity is its reliance on high-quality gas-phase thermochemical data for deriving group equivalents. If no data are available for a given class, then group additivity cannot be applied to that class. For example, new agrochemicals under development at Rohm and Haas are derived from substituted hydrazides. In order to guide synthesis and scale-up of these commercial products, it is useful to be able to predict their reaction thermochemistries. Unfortunately, no experimental gas-phase thermochemical data are available for hydrazides. This prevents direct calculation of heats of reaction and makes it impossible to apply group additivity because a group equivalent for the CO–N–N fragment cannot be derived.

Molecular orbital theory has been successfully applied to compute heats of formation. Most MO calculations fall into one of three basic approaches: (1) ab initio computed isodesmic reactions,[4,5] (2) ab initio energies corrected with group equivalents,[6–9] or (3) direct computation using semiempirical methods such as MNDO,[10,11] AM1,[12] or PM3.[13] In the second approach electronic energies are converted to enthalpies of formation by adding derived atom equivalents for all constituent atoms and subtracting them from the electronic energy.[9] The advantage of MO based approaches is that they can be more generally applied. The trade-off is that, except for semiempirical methods, they can only be applied to relatively small compounds given their computational expense.

I have carried out AM1, isodesmic, and atom equivalent corrected molecular orbital (AECMO) calculations for five derivatives of hydrazide. The accuracy of the AECMO approach for this class of chemistry can be estimated by comparing the full isodesmic and AECMO calculations. In addition I have explored using ab initio computed heats of formation to determine the missing Benson group additivity parameter for hydrazide. This latter approach has two advantages: (1) It is computationally efficient, and (2) it allows us to benefit from the large number of Benson group equivalents which have already been determined.

PROCEDURE

The AM1[12] heats of formation were computed directly using AMPAC.[14] In order to compute heats of formation using only ab initio MO theory, it is necessary to compute a thermochemical cycle. Most commonly this is the heat of reaction for an isodesmic reaction. With the computed heat of reaction and experimental enthalpies of formation for all but one compound in the reaction, it is possible to compute the enthalpy of formation for the remaining reactant or product molecule. For example, eq 1 can be used to compute the heat of formation for **1**.

$$HCONHNH_2 + NH_3 \rightarrow HCONH_2 + NH_2NH_2 \quad (1)$$

1a (cis)   1b (trans)
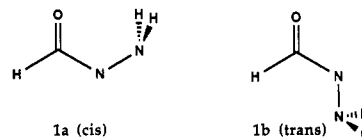
The isodesmic[4,5,15] reactions were computed at a variety of levels from HF/6-31G*//HF/6-31G* up through MP4-(SDTQ)/6-311G**//MP2/6-311G** using Gaussian90.[16] No attempt was made to extend the MP4/6-311G** energies using Pople's G1 theory.[17] The calculated heats of formation were corrected further by applying HF/6-31G* thermal corrections to 298 K.

Heats of formation were also computed using Ibrahim and Schleyer's[9] combined MO group additivity method. This atom equivalent corrected molecular orbital (AECMO) procedure only requires a single calculation for the compound of interest

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Table 1. Total Energies (hartrees) and Heats of Formation (kcal/mol)

structure	HF/6-31G*	MP2/6-311G**	MP4/6-311G**[a]	ΔH_f(expt)
1a	−223.922 7800	−224.755 2126	−224.730 5614	
1b	−223.920 7380	−224.752 1590		
2a	−262.968 4398	−263.978 4018		
2b	−262.964 5962			
3a	−262.951 9775	−263.960 5473		
3b	−262.951 6778	−263.958 4883		
4a	−301.997 5754	−303.184 1229		
4b	−301.995 5138			
5a	−301.979 4698	−303.166 4359		
5b	−301.982 7599	−303.167 9291		
$HCONH_2$	−168.930 7027	−169.551 1990	−169.532 0307	−44.5[b]
CH_3CONH_2	−207.976 0115	−208.773 6038	−208.753 3201	−56.96[b]
NH_2NHCH_3	−150.201 0839	−150.829 1653		22.61[b]
$NH_2N(CH_3)_2$	−189.227 5980	−190.034 8598		20.05[b]
CH_4	−40.1951 719	−40.3980 427	−40.4050 302	−17.8[b]
NH_3	−56.1843 563	−56.4278 760	−56.4280 335	−11.0[c]
CH_2O	−113.866 3313	−114.272 4263	−114.262 6514	−26.0[b]
CH_3NH_2	−95.2098 287	−95.6253 400	−95.6254 249	−5.5[b]
NH_2NH_2	−111.164 9155	−111.618 0438	−111.613 9050	22.8[c]
CH_3CHO	−152.915 9655	−153.498 8299	−153.487 7168	−39.70[c]

[a] Computed at the MP2/6-311G** geometry. [b] Reference 2. [c] Reference 11.

Table 2. Computed Heats of Formation (kcal/mol)

method	1a	2a	3a	4a	5b	$HCONH_2$	CH_3CONH_2
AM1	−18.4	−24.3	−14.3	−19.8	−6.8	−44.7	−50.7
AECMO	−19.4	−30.0	−17.6	−28.2	−16.8	−46.3	−56.8
HF/6-31G*	−17.9	−30.6	−13.7	−26.4	−19.0	−46.0	−55.5
+TC[a]	−17.8	−30.6	−14.4	−26.2	−20.0	−45.1	−56.3
MP2/6-311G**	−19.4	−32.3	−15.9	−29.2	−19.6	−45.8	−55.7
+TC[a]	−19.3	−32.4	−16.6	−29.0	−20.6	−44.9	−56.5
MP4/6-311G**[b]	−18.6					−45.6	−55.8
+TC[a]	−18.5					−44.8	−56.7

[a] Thermal correction to 298 °K at the HF/6-31G* level. [b] Single point at the MP2/6-311G** geometry.

at the HF/6-31G* level. The enthalpy of formation can be computed by subtracting all the atom equivalents for a given compound from its electronic energy. All atom equivalents used in this work came from Ibrahim and Schleyer's paper.[9]

The group additivity parameters were derived by Benson[1] and are taken from a collection compiled by Lowry and Richardson.[3]

PARENT COMPOUND

Heats of formation were calculated for **1** using AM1, AECMO, and ab initio isodesmic calculations. The calculated energies are given in Table 1, and the corresponding heats of formation are given in Table 2. The computed enthalpies of formation for **1** range from −17.8 to −19.8 kcal/mol. This is good agreement given the variety of methodologies employed. As a check, the heats of formation for formamide and acetamide were calculated using the same levels of theory and eq 2. The computed heats of formation for formamide and

$$CH_3CONH_2 + CH_2O \rightarrow HCONH_2 + CH_3CHO \quad (2)$$

acetamide agree well with the experimental values of −44.5 and −57.0 kcal/mol, respectively. For formamide the best agreement with experiment is obtained with AM1 and MP4. For acetamide the best agreement is obtained with AECMO and MP2. In both cases the only serious divergence from experiment is the AM1 ΔH_f for acetamide which is in error by 6.3 kcal/mol. Otherwise all methods are within 2 kcal/mol of experiment.

Hydrazides can adopt two primary conformations (*cis* and *trans*) about the CO–N bond. Normally one might expect
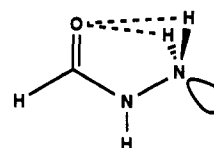

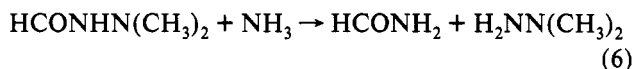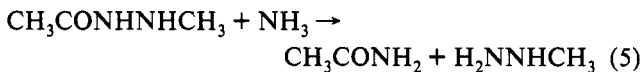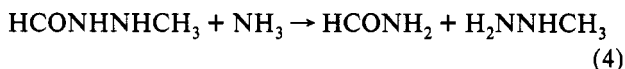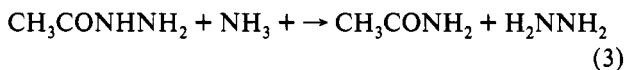**Figure 1.** *Cis* conformer of the parent hydrazide (**1**).

Table 3. HF/6-31G* Computed Dipole Moments (D)

structure	*cis*	*trans*	Δ
1	2.58	4.64	2.06
2	2.69	4.41	1.72
3	2.63	4.64	2.01
4	2.70	4.41	1.71
5	2.87	4.57	1.70

the *trans* conformer to predominate, but in the parent (**1**) *cis* is favored over trans by 1.3 kcal/mol at the HF level and 1.9 kcal/mol at the more sophisticated MP2 and MP4 levels. The origin of this preference is probably not steric. Indeed molecular mechanics calculations using the Dreiding force field[18] favor the *trans* isomer. This argues for an electronic effect which would be absent in the classical force field. Two possibilities present themselves. First, the positively charged terminal amino hydrogens in **1** are positioned in the *cis* isomer, so that they are relatively close to the carbonyl oxygen (2.74 Å) giving the *cis* conformer a favorable, albeit weak, pair of intramolecular hydrogen bonds (Figure 1). Second, the *cis* conformer results in a smaller dipole moment due to better concellation between the terminal N lone-pair dipole and the C=O dipole (Table 3). Inspection of Table 3 shows that the computed dipoles for the *cis* conformers are significantly smaller.

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METHYL SUBSTITUTED DERIVATIVES

Heats of formation were also computed for methyl substituted derivatives of hydrazide, **2–5**. The ab initio heats of formation were calculated using eqs 3–6. The results of these calculations are given in Tables 1 and 2.

$$CH_3CONHNH_2 + NH_3 + \rightarrow CH_3CONH_2 + H_2NNH_2 \tag{3}$$

$$HCONHNHCH_3 + NH_3 \rightarrow HCONH_2 + H_2NNHCH_3 \tag{4}$$

$$CH_3CONHNHCH_3 + NH_3 \rightarrow$$
$$CH_3CONH_2 + H_2NNHCH_3 \tag{5}$$

$$HCONHN(CH_3)_2 + NH_3 \rightarrow HCONH_2 + H_2NN(CH_3)_2 \tag{6}$$
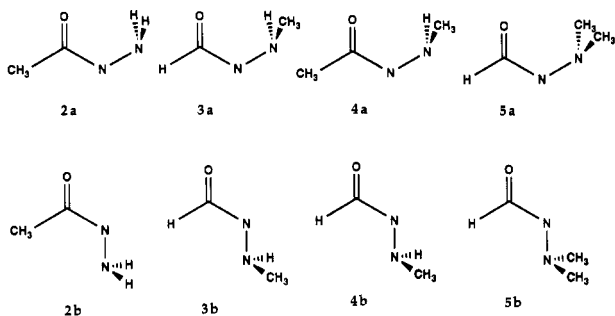
Evaluation of the *cis* and *trans* conformations of **2–5** shows that only the *N,N*-dimethyl derivative (**5**) prefers a *trans* conformation. Otherwise *cis* predominates. This is reasonable since steric crowding in the *cis* conformer is increased significantly moving from **1** to **5**, and since the *cis* conformer in **5** cannot form intramolecular hydrogen bonds such as **1**. Taken together, these factors conspire to invert stability of the *cis* and *trans* conformers when the terminal amino nitrogen is disubstituted. At the MP2 level the *trans* conformer of **5** is 0.9 kcal/mol more stable than the *cis* conformer. In addition to *cis* and *trans* conformers about the CO–N bond, **5** can adopt a variety of conformations due to rotation about the N–N bond. This conformation space was explored systematically at the HF level, and the lowest conformation was found to have the terminal N lone pair essentially eclipsing the N–CO bond.

COMPARISON OF MODELS

The AECMO calculated enthalpies agree well with the thermal energy corrected isodesmic reaction computed enthalpies (Figure 2). The unsigned average error between the HF and AECMO computed enthalpies of formation for seven compounds is within 2 kcal/mol (1.8 kcal/mol). The MP2 and AECMO computed enthalpies of formation are in slightly better agreement with an unsigned average difference in 1.4 kcal/mol. Comparison of the AECMO and MP4 values (for only three compounds) yields a much smaller unsigned average error of 0.8 kcal/mol. It should be pointed out that for these three compounds agreement is much better between AECMO and the isodesmic calculations at all levels of theory. For formamide and acetamide it is possible to compare the computed heats of formation directly with experiment. The comparison is very good. At all levels of theory the isodesmic derived heats of formation are all well within 1 kcal/mol of experiment. The worst agreement between computed and
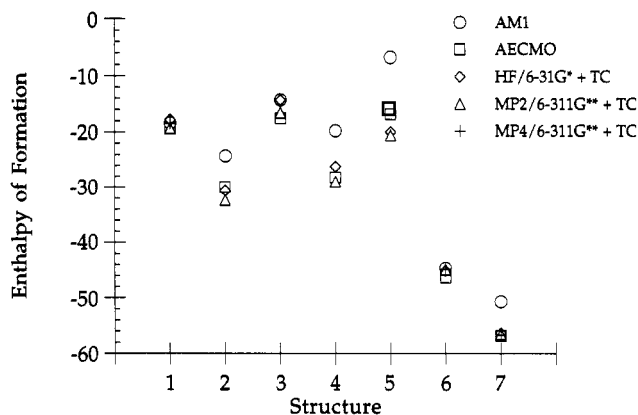
Figure 2. Graphical comparison of computed enthalpies of formation at different levels of theory (formamide and acetamide are compounds **6** and **7**, respectively).

experimentals heats of formation are found with AECMO for formamide and AM1 for acetamide. The latter error is particularly large at 6.3 kcal/mol.

Overall, the AECMO results are encouraging in that this simple approach gives a good approximation to the more time consuming isodesmic reactions (Figure 2). As such, these results support using the AECMO corrected HF/6-31G* energies to compute enthalpies of formation. This is fortunate, because the AECMO calculations require only a single HF/6-31G* calculation instead of the many calculations required to do a proper isodesmic reaction. It is also, of course, much faster to do a relatively simple HF/6-31G* calculation than large basis set correlated calculations such as MP4/6-311G**/ /MP2/6-311G**.

The AM1 heats of formation tend to be consistently more positive than the AECMO or isodesmic values. The most glaring deviations are for **4a** and **5b**. For formamide and acetamide AM1 gives mixed results with errors of 0.2 and 6.3 kcal/mol compared to experiment. This is consistent with reported average errors for AM1.[12] In the absence of experimental evidence it is impossible to say whether the ab initio or semiempirical methods are most in error. Given good agreement at a variety of theoretical levels and the reported average errors[4,9,12,15] for these methods, the MP2 and AECMO computed heats of formation are probably most reliable. It appears that the methyl substituted compounds provide a more difficult challenge for AM1 and the HF isodesmic reactions. These errors may be systematic.

GROUP ADDITIVITY

Even though the AECMO calculations are simpler and less expensive than high-level isodesmic reactions, they are costly. I propose an alternative which builds on Benson's group additivity method and requires fewer MO calculations.

A single group equivalent for N–(N)(CO)(H) is needed to make Benson's group additivity scheme available for substituted hydrazides. This value cannot be derived experimentally due to lack of data for hydrazides, but it can be derived from calculated heats of formation. Given the good performance of the AECMO approach, we have chosen to use AECMO computed heats of formation as data for deriving the N–(N)-(CO)(H) equivalent. One could also use the isodesmic heats of formation and achieve similar results, but they are more expensive to obtain.

This approach can be demonstrated for the N(CO)(H)$_2$ equivalent found in amides. Heats of formation were computed for formamide and acetamide using the AECMO

Table 4. Partial Group Additivity Heats Neglecting N(CO)(N)(H)

structure	partial GA	Benson cis	Benson gauche	computed *cis*
1a	−18.2	1.0[a]		−2.0[c]
1b	−18.2			
2a	−31.5	1.0[a]		
2b	−31.5	1.0		
3a	−18.8	1.0[a]	0.8	−1.3[d]
3b	−18.8			
4a	−32.1	1.0[a]	0.8	
4b	−32.1	1.0		
5a	−20.6	4.0[b]	0.8	1.0[d]
5b	−20.6			

[a] Benson *cis* correction for substituted alkenes. Given that the *cis* isomer is computed to be more stable than *trans*, the Benson *cis* correction has been waved for this conformation. [b] This is the Benson correction when one *cis* group is *tert*-butyl. Given that there is a strong repulsive interaction between the N lone pair and CO the *tert*-butyl correction is probably appropriate in **5a**. [c] Computed at the MP4/6-311G** level. [d] Computed at the MP2/6-311G** level.

Table 5. Benson Heats of Formation (kcal/mol) Calculated with Derived N(CO)(N)(H) Equivalent

structure	model 1	error[a]	model 2	error[a]
1	−16.7	2.7	−17.5	1.9
2	−30.0	0.0	−30.8	−0.8
3	−16.5	1.1	−16.3	1.3
4	−29.8	−1.6	−29.6	−1.4
5	−19.1	−2.3	−17.9	−1.1
av |error|		1.5		1.3
std dev		2.0		1.5

[a] Error relative to the AECMO computed heats of formation.

Figure 3. Comparison of group additivity (model 1) and AECMO computed enthalpies of formation.

Figure 4. Comparison of group additivity (model 2) and AECMO computed enthalpies of formation.

approach (Table 2). These computed heats of formation were then used to solve for N(CO)(H)$_2$. The average N(CO)(H)$_2$ equivalent is computed to be −15.3 kcal/mol, which is in excellent agreement with the actual Benson value of −14.9 kcal/mol. If one can compute a group equivalent for amides using two computed heats of formation, it should be possible to estimate the missing hydrazide equivalent based on five computed heats of formation.

Partial group additivity values are given in Table 4 for compounds **1–5**. The only missing terms are the N–(N)-(CO)(H) equivalents. The most straightforward approach is to determine the value for N–(N)(CO)(H) which leads to the smallest average error for **1–5** as compared to the AECMO calculated enthalpies of formation. The MO calculations show that the most stable conformer for **1–4** is *cis* and for **5** is *trans*. Therefore the Benson steric corrections for *cis* or *trans* double bonds (the amide-like C–N bond is planar) have been replaced with the ad hoc rule that the hydrazide O–C–N–N dihedral is 0° (*cis*) unless the terminal nitrogen is disubstituted in which case it is 180° (*trans*). The average value for N–(N)-(CO)(H) computed in this way is 1.5 kcal/mol. Adding 1.5 kcal/mol to the rest of the group equivalents and applying Benson gauche corrections lead to group additivity estimates for the heats of formation of **1–5** which are labeled model 1 in Table 5. The average unsigned error with respect to the AECMO computed heats of formation is 1.5 kcal/mol (standard deviation = 2.0 kcal/mol). This is reasonably good agreement.

A plot of the AECMO and group additivity (model 1) heats of formation (Figure 3) shows that the parent and dimethyl substituted compounds (**1** and **5**) contribute most of the error. This could be attributed to many factors, including, of course, random variation in the computed heats of formation. Two
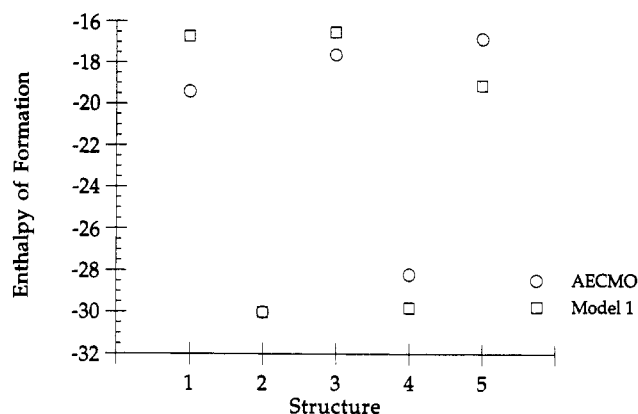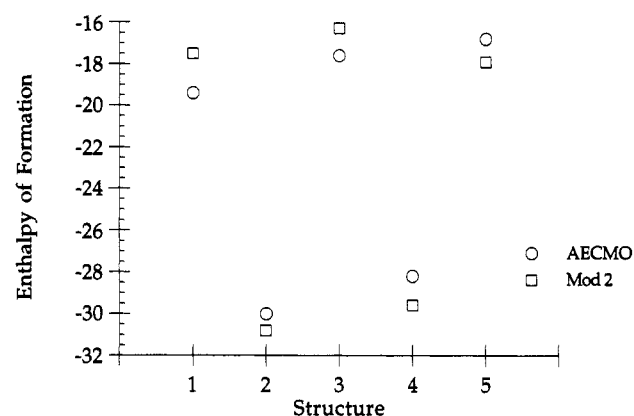
approaches improve the error: modifying the Benson equivalent for C(H)$_3$(N) or applying a *cis/trans* correction. The first was discarded because it meant altering the basic Benson group additivity framework. The second is supportable given the computed energy differences for *cis* and *trans* rotamers of **1** and **5**. The *cis* rotamer of **1** is favored over *trans* by approximately 2 kcal/mol at the MP2 and MP4 levels. Conversely the *trans* rotamer of **5** is favored by 1 kcal/mol at the MP2 level. This has been explained as unfavorable steric interactions overwhelming an apparently favorable electronic interaction in the *cis* rotamer of **5**. The *cis* conformation of **3** is favored over *trans* by an intermediate 1.3 kcal/mol. A similar result would be expected for **4**. As such it makes sense to penalize the *trans* rotamer of **5** by 2 kcal/mol and the *cis* rotamers of **3** and **4** by 1 kcal/mol relative to the *cis* rotamers of **1** and **2**. Adopting this approach (correction = 1.0/terminal N-substitution) gives an even smaller value for N–(N)(CO)(H) of 0.7 kcal/mol and improves the average unsigned error to 1.3 kcal/mol (standard deviation = 1.5 kcal/mol). This is listed in Table 5 as model 2. The fact that this approach reduces the spread between group additivity and AECMO computed heats of formation can be seen in Figure 4.

As with any purely empirical scheme, there are limitless potential approaches for improving the group additivity results beyond deriving a value for N–(N)(CO)(H). More complicated schemes involving multiple *cis* corrections to the group additivity heats of formation not only improves the average error with respect to MO computed heats but can also be used to differentiate between *cis* and *trans* rotamers. The problem with these additions is that they really require more data in order to be well defined. One advantage of using MO

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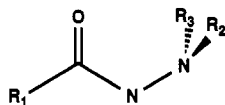
R_1, R_2 and R_3 = any functional group with defined group equivalent.

Figure 5. Structures now computable using Benson's group additivity scheme.

computed heats in lieu of experimentally observed heats is that we can generate more data relatively easily (depending on computing budget). The present level of accuracy is adequate for our applications, so no effort has been made to push the model further.

With the derived group equivalent for N–(N)(CO)(H) in hand it is possible to compute heats of formation for a wide variety of hydrazides (Figure 5) simply and with reasonable expected accuracy. Further with group additivity, unlike the MO calculations, size is not an issue. Even very large systems are reduced to simple pencil and paper calculation.

CONCLUSION

MO computed heats of formation have been determined for five substituted hydrazides at a variety of levels. Comparison of isodesmic computed heats at the HF, MP2, and MP4 levels of theory with heats computed using atom equivalent corrected MF/6-31G* (AECMO) calculations show close agreement. This supports using the AECMO approach to study the thermochemistry of hydrazides.

In addition the computed heats of formation were used to derive the missing Benson group equivalent for N(CO)(N)-(H). This allows one to predict heats of formation for a wide variety of hydrazides using the Benson method. This general approach may be applicable to many industrial and academic problems where reaction thermochemistry is important and where experimental data are sparse or nonexistent. Obvious examples include reaction planning, process development/ scale-up, combustion, and catalysis. In the future theoretical calculations can be expected to become a significant source for thermochemical data and may become the principal source of data for expanding group additivity schemes.[19]

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