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Density Functional Calculations of Solid State Heats of Formation

by

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DENSITY FUNCTIONAL CALCULATIONS OF SOLID STATE HEATS OF FORMATION

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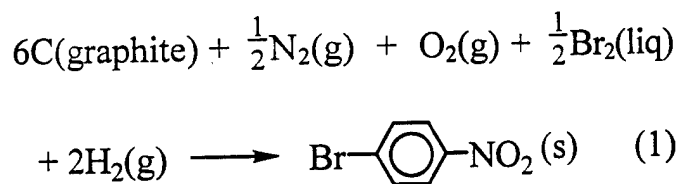
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ABSTRACT

It is now feasible to compute quite accurate gas phase heats of formation for relatively small molecules by means of *ab initio* or density functional techniques and one of several possible approaches: formation reactions, atomization processes or isodesmic reactions. For larger molecules, some empirical correction terms are necessary, even when using density functional methods. Conversion of gas phase values to liquid and/or solid state heats of formation can be done by means of relationships that permit heats of vaporization and sublimation and lattice energies to be predicted from molecular surface electrostatic potentials. We describe in detail a procedure that we have developed, and present and analyze the results obtained for a group of proposed energetic compounds

BACKGROUND

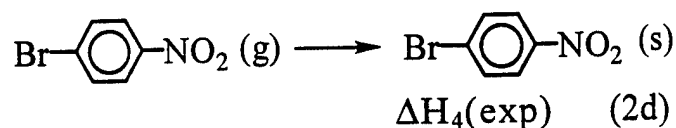
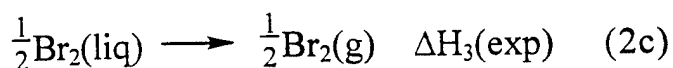
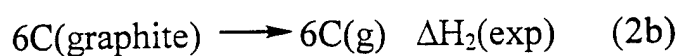
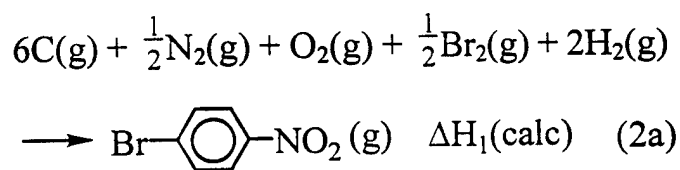
The standard heat of formation of a compound, ΔH_f° , is defined as the enthalpy change associated with its formation from the respective elements, everything being at a pressure of one bar [1]. The elements must be in whatever are their most stable forms at this pressure and the given temperature, which is generally taken to be 25°C (298.15 K). Thus ΔH_f° for *para*-nitrobromobenzene is ΔH for the process,



As this example shows, the reaction in question is typically not chemically realistic. Nevertheless ΔH_f° is a property of great practical importance; a table of such values can permit the calculation of ΔH for a much larger number of chemical reactions, known

or proposed [1]. The latter feature can be particularly appealing, because it means that one can predict the thermochemistry of compounds that have not yet been synthesized. For this reason, and also because the experimental determination of ΔH can sometimes pose a problem, there has been a continuing interest in its computational evaluation. Semi-empirical methods can be quite effective for this purpose [2, 3]; however they are of course limited by the range and flexibility of their parametrization. In this paper our emphasis will be upon *ab initio* and particularly density functional procedures.

The most direct route to computing ΔH_f° would be to calculate the energies E at 0 K of the compound and its elements, all necessarily in the gaseous state, convert these to enthalpies at 298 K to obtain $\Delta H(298\text{ K})$ and then take account of any required phase transformations. Thus $\Delta H_f^\circ(298\text{ K})$ for *para*-nitrobromobenzene would be the sum of the enthalpy changes for the processes:



The needed heats of vaporization or sublimation are generally known experimentally for the elements but perhaps not for the compounds, so that computed heats of formation have most frequently been for the latter in the gaseous state.

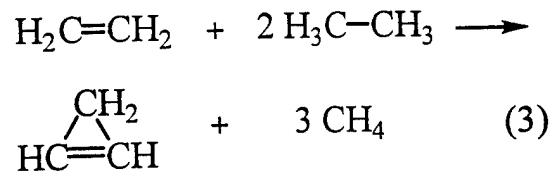
There remains the problem of finding $\Delta H(298\text{ K})$ for the gas phase formation reaction, e.g. eq. (2a). Again, the direct approach is to calculate the energy minima of the elements and the product at 0 K, and to introduce zero-point and thermal corrections to give the enthalpies (and subsequently ΔH) at 298 K. In principle, these corrections require a knowledge of the vibration frequencies [4]; these can be computed, not necessarily at as high a level as the molecular energies since the zero-point and thermal contributions are relatively small in magnitude. An alternative is to estimate the vibrational energies from the molecular stoichiometries [5, 6], which can be done with perhaps surprising accuracy. All of this shall be discussed in more detail in the next section.

If the product molecule and its elements are not small enough to be treated at a very high computational level, then the issue of electronic correlation can become an important problem; ΔH for the formation reaction, e.g. eq. (2a), may not adequately reflect the difference in the correlation

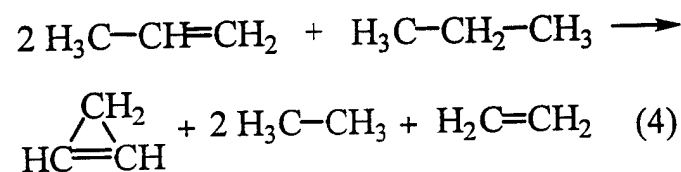
energies of the product and the reactants. This is likely to be particularly significant when the valence electron environments are markedly changed in the course of the reaction, as is typically the case in formation reactions; in eq. (2a), for instance, electrons that were localized on the carbon atom or in multiple bonds in N₂ and O₂ (which furthermore has two of them unpaired) are delocalized in bonds of lower order in the benzene ring and the nitro group. Thus the calculated ΔH may be unacceptably inaccurate. For example, ΔH_f° for NH₂, NH₃ and N₂H₄ can be obtained quite accurately from the formation reaction at the G2 level, whereas the Hartree-Fock and MP2 results are poor [7].

One way to deal with the correlation problem is to avoid the formation reaction, and to devise instead a reaction involving the molecule of interest in which the electronic arrangements in the products are as similar as possible to those in the reactants. This will minimize the change in the total correlation energy and will give, for this process, a more accurate $\Delta H(298\text{ K})$. By setting the latter equal to the difference of the heats of formation of the products and reactants, the desired ΔH_f° can be obtained, provided that reliable values are available for the others. A first step in preserving electronic arrangements in the course of a reaction is to require that the numbers of electron pairs and bonds of each formal type both remain unchanged (isodesmic reaction [4, 8]); even better is to also maintain the

number of atoms with each set of neighbors (homodesmic reaction [9, 10]). For example, isodesmic and homodesmic reactions that could be used to determine the heat of formation of cyclopropene are, respectively [11],



and

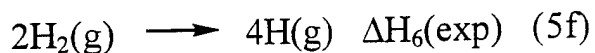
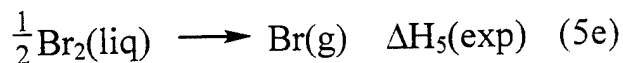
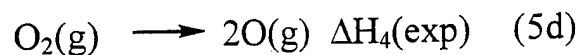
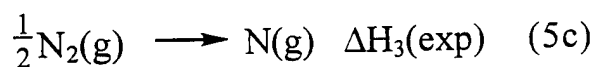
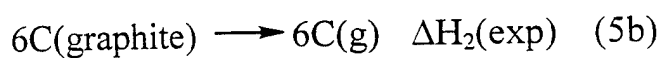
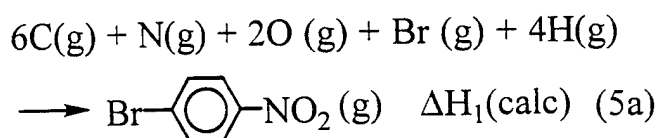


These and related types of reactions have been and continue to be used extensively for calculating heats of formation [11-15]. The computational levels range from Hartree-Fock to correlated *ab initio* and density functional. The success achieved depends, of course, upon devising reactions that do maximally preserve electronic environments and for which the other heats of formation are known accurately.

An alternative approach is to forego the explicit involvement of any chemical reaction and to simply compute the energy of the molecule. This is then converted to ΔH_f° by subtracting semi-empirical terms called "equivalents" which are appropriately modified energies of the chemical groups [16] or individual atoms [2, 17-22] that comprise the molecule. The equivalents are determined by fitting to a data base of

experimental heats of formation. The calculations may be at Hartree-Fock [2, 16-19] or at correlated [20-22] levels. The reliability of the results naturally depends upon the extent and comprehensiveness of the data base and the range of the equivalents; these are designed to reflect the groups or atoms in various chemical environments.

Recent years have brought major advances in computational methodology and processor technology. Using *ab initio* procedures such as G2 and the CBS group, or hybrid density functional methods with large basis sets, it is now possible to calculate with good accuracy (average absolute deviations of 1-3 kcal/mole) the heats of reactions involving molecules with as many as 6-8 first-row atoms [23-28]. It has accordingly become feasible to compute ΔH_f° for such molecules from their formation reactions [28], such as eq. (2a). Another approach is to calculate $\Delta H(298\text{ K})$ for the formation of the molecule from its individual atoms in the gaseous state and then to introduce the experimental enthalpies required to produce the atoms from the respective elements [24, 27]. Thus $\Delta H_f^\circ(298\text{ K})$ for gaseous *para*-nitrobromobenzene would be the sum of the enthalpy changes for the reactions:



In practice, these reactions are usually written in the reverse order, so that eq. (5a) is an atomization process and the sum of the enthalpy changes is $-\Delta H_f^\circ$. Nicolaides *et al* have compared the effectiveness of these two approaches, the formation and the atomization reactions, exemplified by eqs. (2) and (5), for determining G2 heats of formation of a series of small molecules [29]. They found a slight improvement with the second, but pointed out that this may be specific to G2 calculations. In another comparative study, with CBS methods, Curtiss *et al* obtained somewhat better results with isodesmic reactions than with atomization processes [30].

Our interest in computing heats of formation has stemmed from our work in the area of energetic materials (explosives and propellants). In order to predict the detonation performance of an explosive or the thrust produced by a propellant, it is necessary to know the energy released in its decomposition, which in turn depends upon its heat of formation [31-33]. The latter is accordingly essential to the evaluation and characterization of proposed or newly-synthesized energetic compounds. These

are generally solids, composed of organic molecules with typically 15–30 first-row atoms. We have therefore developed a procedure for calculating ΔH_f° with satisfactory accuracy for such systems, in the gaseous, liquid or solid states [34, 35]. This will be discussed in the next section.

CALCULATION OF LIQUID AND SOLID STATE HEATS OF FORMATION

Our procedure is based upon computing $\Delta H(298\text{ K})$ for the formation of the compound from its elements, e.g. eq. (1) [34, 35]. The first step is to calculate the optimized geometries and energy minima at 0 K for the elements and the product molecule, all in the gaseous state. Each molecular energy is converted to the enthalpy at T K (where T is normally 298.15) by assuming ideal behavior and using the corresponding formulas for the

translational, rotational and vibrational contributions [4],

$$E_{\text{trans}} = \frac{3}{2} RT \quad (6)$$

$$E_{\text{rot}} = \frac{3}{2} RT \quad (\text{non-linear molecule}) \quad (7a)$$

or

$$E_{\text{rot}} = RT \quad (\text{linear molecule}) \quad (7b)$$

$$E_{\text{vib}} = \frac{1}{2} h \sum_i \nu_i + N h \sum_i \nu_i \left[\exp(h\nu_i/kT) - 1 \right]^{-1} \quad (8)$$

followed by,

$$H(T) = E(T) + RT \quad (9)$$

In eqs. (6) - (9), ν_i is the vibration frequency of the i^{th} normal mode, N is Avogadro's number, and the other constants have their usual meanings. Once $H(298\text{ K})$

Table 1. Heat of formation correction terms, in kcal/mole.

Atom	Coordination number	BP86/6-31G**	B3P86/6-31+G**
C	4	5.58	5.42
C	3	5.78	3.93
C	2	2.92	0.41
N	3 (planar)	10.71	5.86
N	3 (pyramidal)	2.65	6.92
N	3 (nitro group)	-0.38	1.28
N	2	7.18	6.20
N	1	2.01	3.41
O	2	-3.82	-1.86
O	1	0.36	-0.61

is known for each element and for the product molecule, $\Delta H(298\text{ K})$ can be obtained. If any of the elements are liquids or solids at 298 K and one bar, their experimental heats of vaporization or sublimation are added as in eq. (2). The result is, in principle, the heat of formation $\Delta H_f^\circ(298\text{ K})$ of the product in the gaseous state.

We use a density functional procedure for these calculations, since we do want to take account of electronic correlation and the molecules of interest are normally too large for correlated *ab initio* methods. Our initial work was at the BP86/6-31G** level, the functionals being the Becke (B) for exchange [36] and the Perdew (P86) for correlation [37]. At present, however, we are using Becke's three-parameter hybrid exchange/correlation functional [38], in the form B3P86/6-31+G**, as implemented in the Gaussian 94 code [39].

We have found that these computational levels are not sufficient to produce heats of formation of consistently satisfactory accuracy [34]; the predicted values are generally too low. It was accordingly necessary to introduce a set of additive correction terms, corresponding to the possible coordination states of the carbons, nitrogens and oxygens in the product molecules [34]. The values of these terms, given in Table 1, were determined by fitting to a data base of experimental gas phase heats of formation. Thus, for *para*-

nitrobromobenzene, for example, we would add 23.64 kcal/mole to the sum of the ΔH for eqs. (2a) - (2c), if the B3P86/6-31+G** procedure were used to find ΔH_1 .

Calculating the vibration frequencies can serve two purposes: First, they permit the evaluation of the vibrational contribution to $H(298\text{ K})$, eq. (8), and second, the absence of any imaginary frequencies confirms that the structure corresponds to an energy minimum [4]. The latter is of course an important point when the compound of interest is one that has not yet been synthesized and its molecular thermodynamic stability may be in question. If this is not an issue, however, then the time-consuming frequency calculations can be avoided and the vibrational energy estimated from the molecular stoichiometry [5, 6]. We have shown that E_{vib} can be reproduced to within 1.0 kcal/mole by relationships of the form [6],

$$E_{\text{vib}}(298\text{ K}), \text{ kcal/mole} = C_{\text{H}}n_{\text{H}} + C_{\text{C}}n_{\text{C}} + C_{\text{N}}n_{\text{N}} + C_{\text{O}}n_{\text{O}} + C_{\text{F}}n_{\text{F}} + C_{\text{Cl}}n_{\text{Cl}} + C_{\text{X}} \quad (10)$$

in which n_i is the number of atoms of the i^{th} type in the molecule. The coefficients C_i were determined by fitting to vibrational energies computed at the BP86/6-31G** and B3P86/6-31+G** levels; their values are given in Table 2.

The procedure that has been described predicts gas phase heats of formation with an average absolute error of approximately

Table 2. Coefficients for vibrational energy relationship, eq. (10).

Coefficient	BP86/ 6-31G**	B3P86/ 6-31+G**
C _H	7.26	7.63
C _C	3.87	4.23
C _N	3.90	4.10
C _O	3.23	3.85
C _F	2.99	3.20
C _{Cl}	2.94	3.73
C _X	-5.17	-4.33

3 kcal/mole. In practice, however, and particularly in the area of energetic materials, the compounds of interest are often liquids or solids under normal conditions. The heats of formation of liquids and molecular solids can be obtained from the gas phase values if the heats of vaporization and sublimation are known:

$$\Delta H_f(\text{liquid}, 298 \text{ K}) = \Delta H_f(\text{gas}, 298 \text{ K}) - \Delta H_{\text{vap}}(298 \text{ K}) \quad (11)$$

$$\Delta H_f(\text{solid}, 298 \text{ K}) = \Delta H_f(\text{gas}, 298 \text{ K}) - \Delta H_{\text{sub}}(298 \text{ K}) \quad (12)$$

In recent years, we have shown that a variety of condensed phase properties that depend upon molecular interactions can be related quantitatively to some subset of a small group of computed quantities that characterize the electrostatic potential on a molecular surface [40-42]. These properties have included boiling points and critical constants, solubilities and solvation free energies, diffusion constants, viscosities,

densities, impact sensitivities, lattice energies and heats of phase transformations. It is the last two of these that are relevant in the present context.

The electrostatic potential that is created in the space around a molecule by its nuclei and electrons is given rigorously by eq. (13),

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (13)$$

in which Z_A is the nuclear charge on atom A, located at \mathbf{R}_A , and $\rho(\mathbf{r})$ is the electronic density. For the applications being discussed, we compute $V(\mathbf{r})$ on the molecular surface defined by the 0.001 au contour of $\rho(\mathbf{r})$ [43]. One of the quantities that we use to characterize this surface potential is its total variance, σ_{tot}^2 , which reflects its range, or spread of values; another is an electrostatic balance parameter v . These are defined by eqs. (14) and (15):

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m \left[V_S^+(\mathbf{r}_i) - \bar{V}_S^+ \right]^2 + \frac{1}{n} \sum_{j=1}^n \left[V_S^-(\mathbf{r}_j) - \bar{V}_S^- \right]^2 \quad (14)$$

$$v = \frac{\sigma_+^2 \sigma_-^2}{\left[\sigma_{\text{tot}}^2 \right]^2} \quad (15)$$

$V_S^+(\mathbf{r}_i)$ and $V_S^-(\mathbf{r}_j)$ are the positive and negative values of $V(\mathbf{r})$ on the surface, and \bar{V}_S^+ and \bar{V}_S^- are their averages;

$$\bar{V}_S^+ = \frac{1}{m} \sum_{i=1}^m V_S^+(\mathbf{r}_i) \quad (16)$$

and

$$\bar{V}_S^- = \frac{1}{n} \sum_{j=1}^n V_S^-(\mathbf{r}_j). \quad (17)$$

We use v as a measure of the balance between the positive and negative regions on the surface, the degree to which the molecule is able to interact with others through both its positive and negative surface potentials. As σ_+^2 and σ_-^2 approach each other in magnitude, whether large or small, v approaches its upper limit of 0.250.

We have shown that the heat of vaporization [40] and the heat of sublimation [44] can be expressed by eqs. (18) and (19),

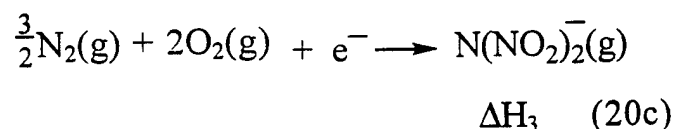
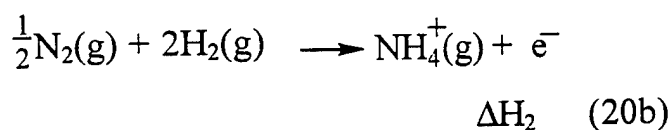
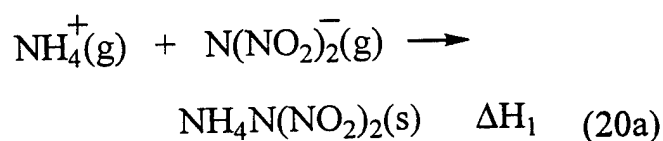
$$\Delta H_{\text{vap}} = a_1 A^{0.5} + a_2 (v\sigma_{\text{tot}}^2)^{0.5} + a_3 \quad (18)$$

$$\Delta H_{\text{sub}} = b_1 A^2 + b_2 (v\sigma_{\text{tot}}^2)^{0.5} + b_3 \quad (19)$$

in which A is the molecular surface area. The coefficients are obtained by fitting to data bases of experimental heats of vaporization and sublimation. They depend of course upon the computational technique being used to calculate $V(\mathbf{r})$; we used Hartree-Fock procedures with small basis sets [40, 44], but Rice *et al* have recently determined them with a different data base and at the B3LYP/6-31G* level [22]; this involved the Lee-Yang-Parr (LYP) correlation functional [45]. In all instances, the average absolute errors are less than 2.8 kcal/mole.

Using heats of vaporization and sublimation produced by eqs. (18) and (19), the heats of formation of liquids and molecular solids can now be obtained from the gas phase values via eqs. (11) and (12). We tested this procedure for a group of five solid compounds [44], computing the gaseous ΔH_f° by the procedure described earlier in this section. The average absolute error in the results was 2.8 kcal/mole.

If the solid compound of interest is ionic rather than molecular, then a somewhat different approach must be used. For example, the heat of formation of ammonium dinitramide, $\text{NH}_4\text{N}(\text{NO}_2)_2$, is the sum of the enthalpies of the following reactions:



ΔH_2 and ΔH_3 , the heats of formation of the ions, may be known experimentally; if not, then they can often be computed quite accurately, since the ions are likely to be small. ΔH_1 is the negative of the lattice enthalpy of the ionic solid. It is readily derived from the lattice energy [46], which

in turn has been expressed analytically, for a given cation, in terms of the properties of the electrostatic potentials on the anions' molecular surfaces [47]:

$$\text{Lattice energy} = aQ + bV_{S,\min} + c\left[A\bar{V}_S^-\right]^2 + d \quad (21)$$

Q is the net charge on the anion and $V_{S,\min}$ is the most negative potential on its surface; A and \bar{V}_S^- have been defined earlier. The coefficients are again determined by fitting to experimental data; there is a separate equation of the form of eq. (21) for each different cation [47].

SOME RESULTS

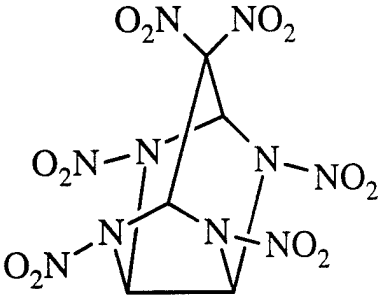
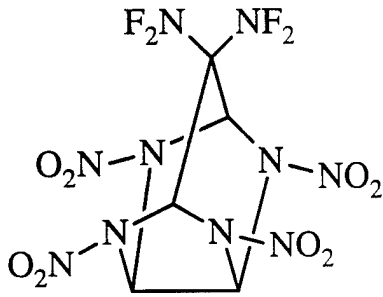
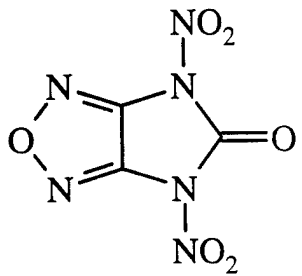
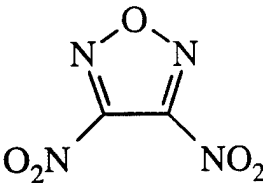
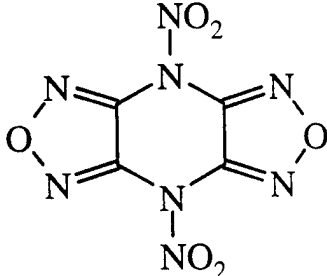
We have now used the procedure presented in the previous section to compute heats of formation for more than 80 compounds. About half of these were for the gaseous phase only, since we could not yet treat liquids and solids; since the development of eqs. (18) and (19), however, we have been producing liquid and solid phase values as well, now for more than 40 compounds. Some of these results have been published [34, 35, 44, 48-51]; the remainder have been communicated to the Office of Naval Research in technical reports. Most of these compounds have not yet been synthesized; prediction of their heats of formation was part of the evaluation process.

As an example, Table 3 gives our results for a group of compounds, 1-7, recently

proposed by Trudell as potential energetic materials [52]. Our computed solid state heat of formation is given for each compound in both kcal/mole and cal/g; the latter units are actually the relevant ones for predicting detonation and/or propellant performance [31-33]. Also listed in the table for each compound except 7 is the heat release that would accompany an idealized decomposition process in which it is converted entirely to the stable gaseous products N_2 , CO or CO_2 , HF and H_2O (and in the case of 4, also O_2). While this may not occur in practice, the corresponding ΔH is an indication of the energy that is potentially available in the compound. It was calculated using our ΔH_f° for each compound and experimental heats of formation for CO, CO_2 , HF and H_2O [53]. Again it is the value of ΔH in cal/g that is important. The heat release is not given for 7, because its stoichiometry is such that there is insufficient oxygen to react with all of the carbon. Finally, in order to provide perspective, Table 3 includes the experimental values for RDX and HMX, which have long been leading military explosives [54, 55].

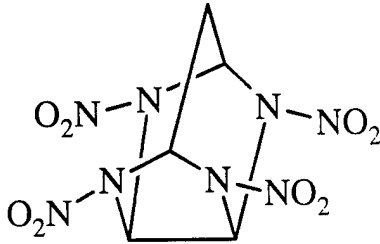
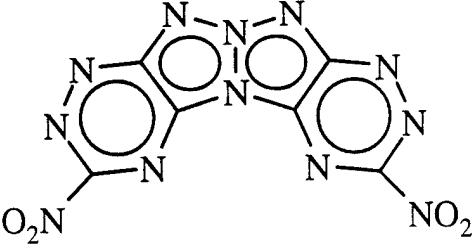
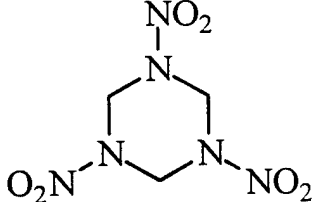
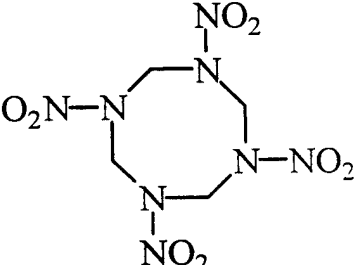
A significant feature of the data in Table 3 is that no two columns show the same trend. For instance, the heat of formation of 1 is greater than that of 4 in kcal/mole but less in cal/g. More important, 5 has a much higher heat of formation than 1-4, in either set of units, but it is below all of them in heat release in cal/g. It is of course notable

Table 3. Computed solid state heats of formation and heat releases.

Compound	ΔH_f (298 K)		Heat release	
	kcal/mole	cal/g	kcal/mole	cal/g
<p>1</p> 	62	157	-648	-1636
<p>2</p> 	54	132	-649	-1590
<p>3</p> 	50	230	-332	-1536
<p>4</p> 	49	304	-237	-1479
<p>5</p> 	126	492	-367	-1433

continued

Table 3. Computed solid state heats of formation and heat releases (continued).

Compound	$\Delta H_f^\circ(298\text{ K})$		Heat release	
	kcal/mole	cal/g	kcal/mole	cal/g
<p>6</p> 	46	150	-351	-1147
<p>7</p> 	260	855		
<p>RDX</p> 	16.9 ^a	76.1 ^a	-270	-1214
<p>HMX</p> 	17.9 ^a	60.4 ^a	-355	-1198

^a Experimental value; ref. 55.

that 1–5 are all above RDX and HMX in heat release in cal/g.

It is obvious that a positive heat of formation is an advantage with regard to heat release upon decomposition. It should be recognized, however, that a negative ΔH_f° does not preclude the liberation of a considerable amount of energy. For example, our computed $\Delta H_f^\circ(298\text{ K})$ for

1,1-dinitro-2,2-diaminoethylene is -27 kcal/mole [51]; however its calculated heat release is -955 cal/g.

SUMMARY

Computational methodology, software and hardware have now improved to the point that gas phase heats of formation can be computed at a high level of accuracy for

molecules with as many as 6–8 first row atoms without resorting to empirical corrections. The latter are still necessary for large molecules, however, even when density functional procedures are used. In this paper, we have discussed in detail our approach, in which the ΔH of the formation reaction is modified in accordance with the types of carbons, nitrogens and oxygens in the molecule [34]; the procedure of Rice *et al* [22], which has also been applied to energetic compounds, uses atom equivalents. In another treatment of large systems, Cioslowski *et al* employ both atom and bond equivalents [56]; the latter concept has been used extensively for energetic molecules by Melius [57], and very recently has been explored by Petersson *et al* [27].

The gas phase heat of formation is very often not the desired final result, since practical interest is often in the liquid or solid phase compound. We have developed techniques for predicting heats of vaporization [40] and sublimation [44] and lattice energies [47] from the electrostatic potentials on molecular and ionic surfaces. It then becomes possible to obtain the heats of formation of liquids and solids, both molecular and ionic, from gas phase values. This has now been done for a large number of energetic compounds by us and by Rice *et al* [22]. Accordingly it is now feasible to compute, with generally satisfactory accuracy, the heats of formation of a wide array of gaseous, liquid and solid compounds of practical chemical interest.

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