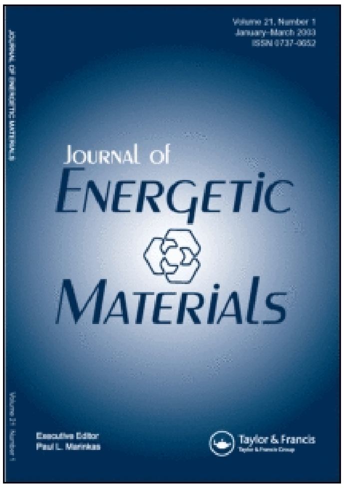

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A systematic procedure for estimating the standard heats of formation in the condensed state of non aromatic polynitro-compounds

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A SYSTEMATIC PROCEDURE FOR ESTIMATING THE STANDARD HEATS OF FORMATION IN THE CONDENSED STATE OF NON AROMATIC POLYNITRO-COMPOUNDS

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ABSTRACT

An additive method for predicting the standards heats of formation at 298 K of aliphatic and alicyclic polynitro-compounds is described. It consists in three steps (i) the evaluation of the enthalpy of formation in the gaseous state (ii) the estimation of the enthalpy of vaporization for a liquid or enthalpy of sublimation for a solid and (iii) the calculation of interaction terms, mainly between NO_2 groups.The uncertainty on predicted values are generally within a few kcal/mol. As an example of application, it is shown that the theoretical specific impulse of high-energy solid propellants can be calculated with a relative uncertainty less than 1 %.

INTRODUCTION

The heat content of an energetic material in the liquid or solid state is represented by the value of its enthalpy of formation, ΔHf°_{c}. The knowledge of such a quantity is required to calculate any performance in propulsion or explosive science. At present time, there is a considerable interest in new high energy oxidizers for solid propellants and new high explosives, especially polynitro cage molecules[1] and nitramines[2] but few of them have been synthetized until then. Consequently, the evaluation of ΔHf°_{c} for numerous target compounds appears to be of a great utility before their tentative synthesis in order to ascertain, in the limits of reasonable error, the expected theoretical performance.

The rigorous direct calculation of ΔHf°_{c} for compounds from their molecular structure including only the number of atoms in the molecule, their nature and connectivity, is a formidable task since it should be treated using quantum mechanics ab initio methods, what is far beyond the current possibility of supercomputers. Consequently, semi-empirical molecular orbital techniques, such as MINDO/3, MNDO or AM1, may be favourably applied as they use a reasonable amount of computer time. However, some of them suffer from large errors, as shown by Davis et al.[3] and, moreover, the results can only be obtained in the gas phase. This is the reason why simpler methods are often employed, that are practically always group additivity methods. Unfortunately, most of them do not provide ΔHf°_{c} either but, as for the semi-empirical molecular orbital techniques, only the heat of formation in the gaseous state, ΔHf°_{g}, the most popular being Benson's scheme[4-6]. Still, some have been applied to compounds in the liquid or solid state[7-12], the calculation being done either with Benson groups only[7] or with Benson groups and additive interaction increments[8-11]. In the reference[12], the procedure is slightly different since the author first estimates the enthalpy of combustion ΔH_c° starting from an equivalent carbon chain length (which includes group increments) and then uses a linear relation between $\Delta H_{f_c}^\circ$ and ΔH_c°. Although these techniques of evaluation generally show a satisfactory agreement between experimental and calculated values, they suffer, as a major drawback, from their limited range of validity. The most useful method for the present purpose, the calculation of $\Delta H_{f_c}^\circ$ for aliphatic and polycyclic nitro-compounds, seems to be the procedure described in the paper of Kizin and Lebedev[10] where the heats of formation of some aliphatic nitro-compounds are calculated as the sum of Benson increments (for the solid state) and interactions between NO_2 groups. But as neither aliphatic molecules containing NO_2 and NNO_2 groups nor polycyclic ones can be evaluated, it is proposed here to estimate the heat of formation of <u>any</u> non-aromatic C, H, O, N nitro-compound in the condensed state as the difference between the heat of formation in the gaseous state and the heat of sublimation ΔH_S (for a solid) or heat of vaporization ΔH_V (for a liquid), plus correction terms for interactions between some atoms and/or atom groups. This idea, which is the second logic possibility for the calculation of $\Delta H_{f_c}^\circ$ (the first one being a direct calculation of the heat of formation in the condensed state by a group additivity method) is not new but its application to the compounds of interest has not been encountered in the literature. In this paper, we try to fill this gap and set forth in detail a general procedure for the evaluation of ΔHf°_{c}. Some instances are given and the results discussed. Lastly, as an example of application, the technique is shown to permit a realistic estimation of the theoretical performance of high energy solid propellants.

THE METHOD

The calculation of ΔHf°_{c} is carried out in the more general way with the relations :

$$\Delta Hf^{\circ}_{c} = \Delta Hf^{\circ}_{g} - \Delta H_v + \Delta in \qquad \text{(liquid)} \qquad (1)$$

$$\Delta Hf^{\circ}_{c} = \Delta Hf^{\circ}_{g} - \Delta H_s + \Delta in \qquad \text{(solid)} \qquad (2)$$

In these expressions, Δin represents the sum of interaction terms between some specific atoms or atom groups. For most compounds, its value can be neglected in comparison to other term value in (1) and (2) except, in particular, for nitro-compounds where strong interactions between NO_2 groups must be accounted for in the estimation of ΔHf°_{c}. Let us note that Δin has been taken identical for liquid and solid state.

The terms ΔHf°_{g}, ΔH_V, ΔH_S and Δin are calculated as follows.

1 - Calculation of ΔHf°_{g}

The Benson group additive method is used with published increment values [4,5]. In the case when a Benson group is missing, it is, if possible, extrapolated or interpolated from known values of "adjacent" groups. Otherwise thermochemical data literature is searched to find the measured heat of formation in the gaseous state of a reference compound from which the group value can be derived. If a measured value of the reference compound is absent, its gaseous heat of formation can be determined by quantum mechanical calculations in the last resort[13]. For ring and polycyclic compounds, strain energy corrections are applied, their values being taken out firstly of references[4, 5] and secondly of references[14, 15]. If the correction term for a polycyclic molecule cannot be found by the preceding means, its value is estimated as the sum of the strain energies of the individual cycles which make up the molecule skeleton[15, 16]. For example, the strain energy of octanitrocubane, being taken equal to cubane's one, may be considered as the sum of the strain energies of six butane rings.

2 - Calculation of ΔH_v and ΔH_s

A - Calculation of ΔH_v

The estimation of ΔH_v and ΔH_s is based on the method of Sastri et al.[17, 18] which gives the heat of vaporization of C, H, N, O, S, X compounds (X = halogen) at the normal boiling point, ΔH_{vb}, by the expression :

$$\Delta H_{vb} = H_{vo}[1 - T_b/T_c]^n \tag{3}$$

where H_{vo} is the sum of the structure increments for the heat of vaporization, T_b the normal boiling point, T_c the critical temperature and n is nearly constant (it depends slightly upon T_b/T_c). The values of T_b and T_c can be found by Lydersen semi-empirical increment method[18,19]. Combining (3) with Thiesen correlation[18],

$$\Delta H_v(T) = k(1 - T/T_c)^n \tag{4}$$

where ΔH_v (T) is the heat of vaporization at temperature T and k a constant, we get, for T = 298 K and n = 0.38 (the most common value) :

$$\Delta H_v \equiv \Delta H_v(298) = H_{vo}\left(1 - \frac{298}{T_c}\right)^{0.38} \tag{5}$$

To summarize, the calculation of ΔH_v is carried out as follows :

a - evaluation of T_c with the help of Lydersen method and structure increment tables from[18, 19].

b - evaluation of H_{vo} from the tables published by Sastri et al.[17,18], where only the increment value of NO_2 for aliphatic and alicyclic compounds has been modified from 8.6 kcal/mol to 4 and 5 kcal/mol respectively.

c - calculation of ΔH_v with equation (5).

B - Calculation of ΔH_s

The estimation of ΔH_s is, a priori, more difficult since no method can be found in the literature. Consequently, we have to follow an indirect way starting from the fact that a heat of sublimation may be considered to be the sum of a heat of fusion ΔH_{f_u} and a heat of vaporization ΔH_v, even though liquid cannot exist at the pressure and temperature in question[19]. The heat of vaporization can be given by equation (5). On the other hand, attempts to obtain general correlations between the enthalpy of fusion and structure of molecules have been unsuccessful in spite of a theoretical treatment presented by Bondi[20] who related the entropy of fusion of molecular crystal to structure. But taking into consideration the remark of Reid et al.[19] that the heat of fusion is usually less than one-third of the heat of vaporization, ΔH_{f_u} is roughly set equal to one-quarter of ΔH_v, leading to

$$\Delta H_s = 5/4\, \Delta H_{vo} \left(1 - \frac{298}{T_c}\right)^{0.38} \qquad (6)$$

Originally, ΔH_s was calculated that way. Now if we note (i) that $(1 - 298/T_c)^{0.38}$ changes from 0.77 to 0.87 when Tc is varied in the approximate range of interest 600 K - 950 K so that $0.96\, H_{vo} \leq \Delta H_s \leq 1.08\, H_{vo}$ and (ii) considering all the uncertainties cumulated on ΔH_s, the heat of sublimation may be quite simply estimated by

$$\Delta H_s \simeq H_{vo} \qquad (7)$$

To summarize, the value of ΔH_s, given by equality (7), will be used throughout this paper, the uncertainty on ΔH_s being admittedly no more than a few kcal/mol.

3 - Calculation of Δin for nitro-compounds

All the interactions have been put into seven groups, according to the nature of the atom (carbon, nitrogen or oxygen) linked to NO_2, for NO_2 - NO_2 interactions, or to the nature of the atoms (oxygen or nitrogen) interacting with NO_2. The representation and value of each kind of interaction is given in Table 1 where the double-headed arrow symbolizes the interaction itself and the double parenthesis, any carbon, nitrogen or oxygen atom. Note that interactions beyond Δ 1-3 for group IV, Δ 1-5 for group V, and Δ 1-4 for the others are not taken into account, their values being considered as negligibly small.

TABLE 1. Individual Interaction Terms in Nitro-compounds.

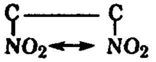
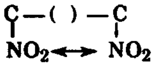
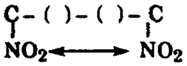
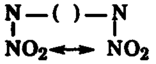
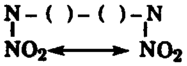
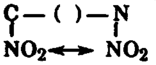
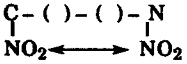
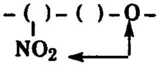
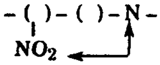
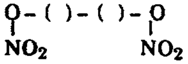
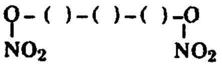
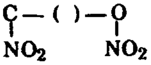
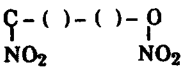
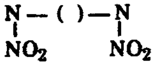
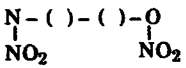
Nature of interaction	Symbol	Value (in kcal/mol)
	Group I	
 $\begin{array}{ccc} C & \text{———} & C \\ \vert & & \vert \\ NO_2 & \longleftrightarrow & NO_2 \end{array}$	Δ 1-2 C-C	5
 $\begin{array}{ccc} C & \text{—(\ )—} & C \\ \vert & & \vert \\ NO_2 & \longleftrightarrow & NO_2 \end{array}$	Δ 1-3 C-C	4
 $\begin{array}{ccc} C & \text{-(\ )-(\ )-} & C \\ \vert & & \vert \\ NO_2 & \longleftrightarrow & NO_2 \end{array}$	Δ 1-4 C-C	2
	Group II	
 $\begin{array}{ccc} N & \text{—(\ )—} & N \\ \vert & & \vert \\ NO_2 & \longleftrightarrow & NO_2 \end{array}$	Δ 1-3 N-N	6
 $\begin{array}{ccc} N & \text{-(\ )-(\ )-} & N \\ \vert & & \vert \\ NO_2 & \longleftrightarrow & NO_2 \end{array}$	Δ 1-4 N-N	3
	Group III	
 $\begin{array}{ccc} C & \text{—(\ )—} & N \\ \vert & & \vert \\ NO_2 & \longleftrightarrow & NO_2 \end{array}$	Δ 1-3 C-N	5
 $\begin{array}{ccc} C & \text{-(\ )-(\ )-} & N \\ \vert & & \vert \\ NO_2 & \longleftrightarrow & NO_2 \end{array}$	Δ 1-4 C-N	2.5
	Group IV	
 $\begin{array}{cccc} -(\ )- & (\ )- & O & - \\ \vert & & \uparrow & \\ NO_2 & \longleftarrow & \lrcorner & \end{array}$	Δ 1-3 (O)	1.5
 $\begin{array}{cccc} -(\ )- & (\ )- & N & - \\ \vert & & \uparrow & \\ NO_2 & \longleftarrow & \lrcorner & \end{array}$	Δ 1-3 (N)	1
	Group V	
 $\begin{array}{ccc} O & \text{-(\ )-(\ )-} & O \\ \vert & & \vert \\ NO_2 & & NO_2 \end{array}$	Δ 1-4 O-O	3
 $\begin{array}{ccc} O & \text{-(\ )-(\ )-(\ )-} & O \\ \vert & & \vert \\ NO_2 & & NO_2 \end{array}$	Δ 1-5 O-O	1

TABLE 1 (continued).

Nature of interaction	Symbol	Value (in kcal/mol)
	Group VI	
 $\underset{NO_2}{C}-(\ )-\underset{NO_2}{O}$	Δ 1-3 C-O	5
 $\underset{NO_2}{C}-(\ )-(\ )-\underset{NO_2}{O}$	Δ 1-4 C-O	2.5
	Group VII	
 $\underset{NO_2}{N}-(\ )-\underset{NO_2}{N}$	Δ 1-3 N-O	6
 $\underset{NO_2}{N}-(\ )-(\ )-\underset{NO_2}{O}$	Δ 1-4 N-O	3

To find the values of the individual interaction terms, it would have been natural to derive them from a set of known values of heats of formation for reference compounds but as few were at disposal, it was proceeded in a different way. Values for group I were taken out from the paper of Kizin and Lebedev[10] and rounded off whereas, in group IV, the value for Δ 1-3 (O) was chosen equal to 1.5 kcal/mol following Kustova et al.[9] and the value of 1 kcal/mol was assigned to the second term of group IV (Δ 1-3 (N)), nitrogen being less electronegative than oxygen. For group II and III, values were found combining appropriate terms of groups I and IV roughly in a linear way (for example, Δ 1-3 C-N = Δ 1-3 C-C + Δ 1-3 (N) = 5 kcal/mol) and modifying slightly some of them to get a best fit with experimental values of $\Delta H f^{\circ}_{c}$ for some compounds given in the next section. Values in group VII and group VI have been taken equal to those of group II and group III respectively whereas, in group V, the value of Δ 1-4 O-O have been chosen identical to the value of Δ 1-4 N-N and the value of Δ 1-5 O-O have been adjusted to fit the experimental values for some compounds.

Finally Δin is obtained as the sum of the different individual terms. If we take the example of octanitrocubane in the condensed state, we can write :

$$\Delta\text{in (octanitrocubane)} = 12\,\Delta\,1\text{-}2\ \text{C-C} + 12\,\Delta\,1\text{-}3\ \text{C-C} + 4\,\Delta\,1\text{-}4\ \text{C-C} = 116\ \text{kcal/mol.}$$

RESULTS AND DISCUSSION

The method has been applied to a large variety of nitro- compounds mainly in the solid state. In Table 2, their structures or formulas are represented and their standard heats of formation at 298 K, both calculated and experimental, given.

For compounds in the solid state, the simple examination of Table 2 shows that agreement is generally good between measured and estimated values of $\Delta H_{f_c}^{\circ}$. Except for compounds n° 3, 15, 16, 17 and 34, the absolute error does not go beyond a few kcal/mol. In particular, this agreement is quite satisfying for cyclic compounds for which no other precise method of calculation can be found in the literature.

Some of the larger divergences for aliphatic molecules can be explained. If we compare the structures of compounds n° 3 and n° 4, we see they differ only by 1 CH_2 group in the carbon chain. As the inclusion of 1 CH_2 group lowers $\Delta H_{f_g}^{\circ}$ (since the corresponding Benson group

TABLE 2. Standard Heats of Formation at 298 K of Nitro-compounds in the Condensed State (in kcal/mol).

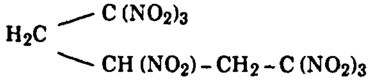
Compound	n°	ΔHf_c° calc.	ΔHf_c° exp.	ΔHf_c° calc. – ΔHf_c° exp.	Ref.
			Solid state		
$(NO_2)_3C-CH_2-OH$	1	- 65.1	- 62.3	- 2.8	21
$(NO_2)_3C-CH_3$	2	- 25	- 26.9	+ 1.9	21
$(H_3C)_2-C(NO_2)-C(NO_2)_2-CH_3$	3	- 68.7	- 79.2	+ 10.5	21
$(H_3C)_2-C(NO_2)-C(NO_2)_2-CH_2-CH_3$	4	- 75.1	- 69.4	- 5.7	21
$H_3C-C(NO_2)_2-C(NO_2)_2-CH_3$	5	- 49.1	- 43.5	- 5.6	21
$(NO_2)_3C-(CH_2)_2-CH_2NO_2$	6	- 39.7	- 45.3	+ 5.6	21
$(NO_2)_2CH-CH_2-C(NO_2)_2CH_3$	7	- 47.9	- 51.6	+ 3.7	10
$(NO_2)_3C-C(NO_2)_2-CH_3$	8	- 16.9	- 13.6	- 3.3	10
$(NO_2)_3C-C(NO_2)_3$	9	+ 20.2	+ 20.4	- 0.2	10
 $H_2C\begin{cases}C(NO_2)_3\\CH(NO_2)-CH_2-C(NO_2)_3\end{cases}$	10	- 33.4	- 36.7	+ 3.3	21

TABLE 2 (continued)

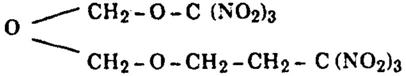
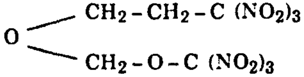
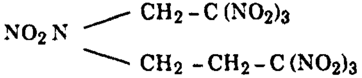
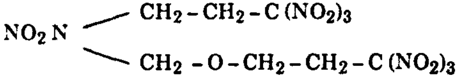
 $O(CH_2-O-C(NO_2)_3)(CH_2-O-CH_2-CH_2-C(NO_2)_3)$	11	- 141.9	- 142.7	+ 0.8	9
 $O(CH_2-CH_2-C(NO_2)_3)(CH_2-O-C(NO_2)_3)$	12	- 100.4	- 96.1	- 4.3	21
$HN-[H_3C-C(NO_2)_2-CH_2]_2$	13	- 68.8	- 63.4	- 5.4	21
$NO_2N-[H_3C-C(NO_2)_2-CH_2]_2$	14	- 51.7	- 55.4	+ 3.7	21
$HN-[(NO_2)_3C-CH_2]_2$	15	- 22.4	- 8	- 14.4	21
$NO_2N-[(NO_2)_3C-CH_2]_2$	16	+ 2.7	- 6.7	+ 9.4	21
 $NO_2N(CH_2-C(NO_2)_3)(CH_2-CH_2-C(NO_2)_3)$	17	- 11.3	- 21.3	+ 10	21
 $NO_2N(CH_2-CH_2-C(NO_2)_3)(CH_2-O-CH_2-CH_2-C(NO_2)_3)$	18	- 69.6	- 72.4	+ 2.8	9

TABLE 2 (continued)

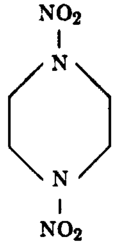
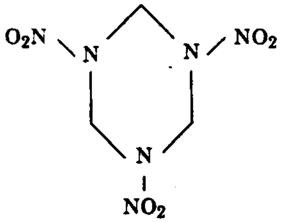
$NO_2N-[CH_2-O-CH_2-C(NO_2)_3]_2$	19	-89.2	-92.6	+3.4	9
	20	-8	-12.7	+4.7	21
	21	+18.5	+15.9	+2.6	21

TABLE 2 (continued)

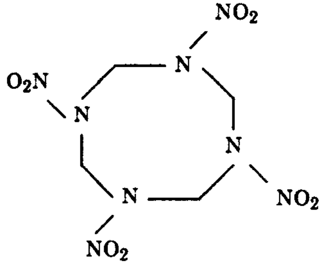
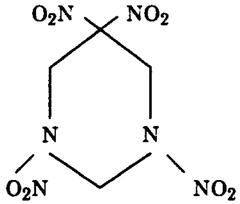
	22	+ 26	+ 21	+ 5	22
	23	+ 0.1	+ 2	- 1.9	23

TABLE 2 (continued)

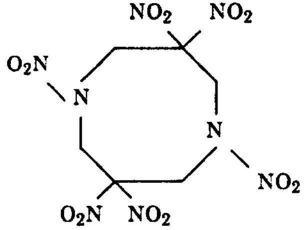
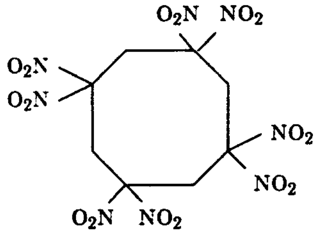
	24	- 10	- 5		- 5	23
	25	- 48.3	-	-	-	-

TABLE 2 (continued)

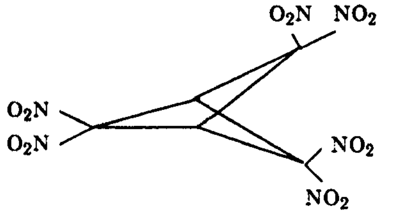
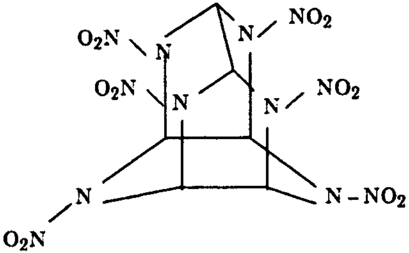
	26	+ 43	
	27	+ 99.3	

TABLE 2 (continued)

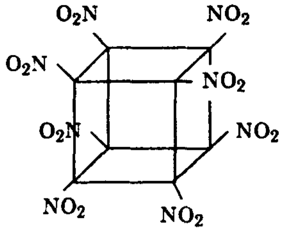
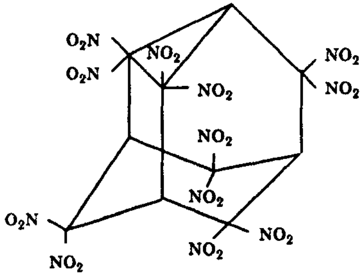
	28	+ 98.9	-		
	29	+ 40.2	-	-	

TABLE 2 (continued)

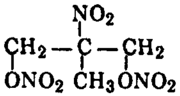
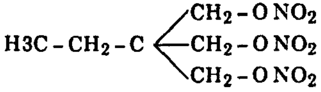
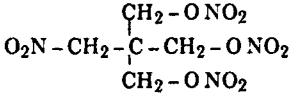
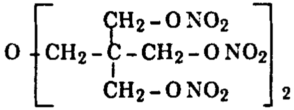
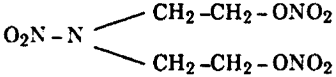
 $CH_2(ONO_2)-C(NO_2)(CH_3)-CH_2ONO_2$	30	- 87.9	- 89.4	+ 1.5	21
 $H3C-CH_2-C(CH_2-ONO_2)_3$	31	- 115.1	- 114.8	- 0.3	24
 $O_2N-CH_2-C(CH_2-ONO_2)_3$	32	- 126.8	- 128.7	+ 1.9	21
 $O[CH_2-C(CH_2-ONO_2)_3]_2$	33	- 235.3	- 234.1	- 1.2	21
 $O_2N-N(CH_2-CH_2-ONO_2)_2$	34	- 64.1	- 75.4	+ 11.3	24
			Liquid state		
see above	1	- 61.6	- 59.7	- 1.9	21
" "	2	- 22.5	- 23.2	- 0.7	21

TABLE 2 (continued)

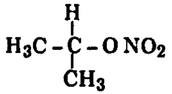
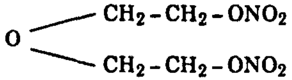
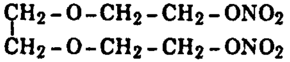
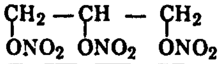
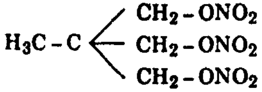
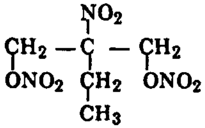
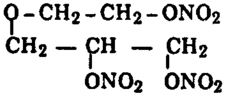
" "	5	- 4.6	- 40.1	- 5.9	21
" "	6	- 36.5	- 42.8	+ 6.3	21
" "	10	- 29.5	- 33.7	+ 4.2	21
H_3C-ONO_2	35	- 34.9	- 35.2	+ 0.3	24
$H_3C-CH_2-ONO_2$	36	- 44.2	- 42.8	- 1.4	24
$H_3C-CH_2-CH_2-ONO_2$	37	- 50.3	- 51.3	+ 1	24
 $H_3C-\overset{H}{\underset{CH_3}{C}}-ONO_2$	38	- 54.5	- 54.9	+ 0.4	24
	39	- 107.4	- 98.4	- 9	24
 $CH_2-O-CH_2-CH_2-ONO_2$ $CH_2-O-CH_2-CH_2-ONO_2$	40	- 150.0	- 144.9	- 5.1	24
 $\underset{ONO_2}{CH_2}-\underset{ONO_2}{CH}-\underset{ONO_2}{CH_2}$	41	- 88.8	- 88.6	- 0.2	21

TABLE 2 (continued)

	42	- 105.2	- 106.0	+ 0.8	24
	43	- 91.2	- 87.8	- 3.4	21
	44	- 135.2	- 128.2	- 7.2	21

$C\text{–}(H)_2(C)_2$ is equal to - 4.95 kcal/mol) and simultaneously increases the heat of sublimation (the increment for H_{VO} is 1.44 kcal/mol), it should be expected the heat of formation in the solid state for compound n° 4 to be approximately lower by 4.95 + 1.44 ≈ 6 kcal/mol than the heat of formation of compound n° 3. Now, on the contrary, measured $\Delta H^{\circ}_{f_c}$ for n° 4 is higher by 10 kcal/mol than measured $\Delta H^{\circ}_{f_c}$ for n° 3. Consequently large errors in the experimental values of $\Delta H^{\circ}_{f_c}$ for these two compounds may exist. For molecules n° 16 and 17, the absolute errors on $\Delta H^{\circ}_{f_c}$ are respectively + 9.4 and + 10 kcal/mol. If we note that the calculation of Δin for these compounds is equal to 6 Δ 1-3 C-N = 30 kcal/mol for the former and 3 Δ 1-3 C-N + 3 Δ 1-4 C-N = 22.5 kcal/mol for the later, we may infer that the Δ values are probably somewhat too high by approximately 1 kcal/mol . This hypothesis seems acceptable since the heats of formation for compounds n° 14 and n° 18, for which Δ 1-3 C-N and Δ 1-4 C-N terms exist, would also be more accurate with lower Δ values. But, on the contrary, a decrease in Δ 1-3 C-N and Δ 1-4 C-N would lead to less accurate results for cyclic compounds. So the best way to operate would have been to give separate values for aliphatic and alicyclic compounds. This has not been done because of a lack of sufficient experimental data. Finally, the only higher divergences to be left unexplained are those of compounds n° 15 and 34. For polycyclic compounds (n° 26 to 29), no comparison between experimental and calculated values has been done, the synthesis of these molecules having not appeared in the literature. In the future, this comparison should be most interesting to check more widely the validity of the method because of the numerical importance of numerous interactions NO_2 - NO_2 "boosting" the heats of formation to high positive values.

For the liquids, fewer examples can be found in the literature for comparison. Again Table 2 shows a good agreement between estimated and experimental values within a few kcal/mol.

APPLICATION

In rocket propulsion engineering, the most useful performance parameter is the theoretical specific impulse I_s defined as the thrust delivered per unit flow weight of propellant consumed, and generally expressed in seconds. I_s being dependent on the heat of formation of the propellant, one may ask oneself how much inaccuracy ΔI_s the uncertainty on calculated $\Delta H_{f_c}^{\circ}$ can induce on the value of I_s or, in other words, is the uncertainty on $\Delta H_{f_c}^{\circ}$, $\Delta\ (\Delta H_{f_c}^{\circ})$, not too large to get an acceptable value for the uncertainty on I_s. To answer this question, we use the expression of Gordon[25] which relates ΔI_s (in seconds) to $\Delta\ (\Delta H_{f_c}^{\circ})$ (in kcal/kg) by the equation :

$$\Delta I_s = 43.5 \left(\frac{\Delta (\Delta H_{f_c}^{0})}{I_s} \right) \left(1 - \frac{T_e}{T_{ch}} \right) \qquad (8)$$

where T_e and T_{ch} are the temperatures of the combustion products, in kelvins, respectively at the nozzle exit and in the chamber.

The parameters T_e, T_{ch}, and I_s are specific of each kind of propellant but for the present purpose we need only orders of magnitude.

Here we will choose T_e = 2000 K, T_{ch} = 3800 K, and I_s = 270 s. These values roughly characterize the most energetic propellants currently employed. Moreover, we suppose that solid state compounds in Table 2 are incorporated in propellants as oxidizers with a mass proportion of 70 %. Under these conditions, the values of ΔI_s are calculated putting in equation (8) the values of $\Delta(\Delta H^{\circ}_{f_c}) = \Delta H^{\circ}_{f_c}$ calc: - $\Delta H^{\circ}_{f_c}$ exp., taken from Table 2, multiplied by 0.7 and converted in kcal/kg. The results are reported in Table 3.

TABLE 3. Uncertainty ΔI_s on the Theoretical Specific Impulse I_s (in seconds) with Solid State Compounds of Table 2, as Oxidizers.

Compound number	$\Delta(\Delta H^{\circ}_{f_c})$ (kcal/kg)	ΔI_s (s)	Compound number	$\Delta(\Delta H^{\circ}_{f_c})$ (kcal/kg)	ΔI_s (s)
1	- 15.4	- 0.8	16	+ 24.2	+ 1.3
2	+ 11.5	+ 0.6	17	+ 24.9	+ 1.3
3	+ 50.7	+ 2.7	18	+ 6.3	+ 0.3
4	- 25.8	- 1.4	19	+ 7.6	+ 0.4
5	- 23.5	- 1.3	20	+ 4.7	+ 0.3
6	+ 23.5	+ 1.3	21	+ 11.7	+ 0.6
7	+ 15.5	+ 0.8	22	+ 16.9	+ 0.9
8	- 12.3	- 0.7	23	+ 7.5	+ 0.4
9	- 0.7	- 0.03	24	- 13	- 0.7
10	+ 8.5	+ 0.5	30	+ 6.7	+ 0.4
11	+ 2	+ 0.1	31	- 1.1	- 0.1
12	- 11.5	- 0.6	32	+ 6.0	+ 0.3
13	- 19.2	- 1	33	- 2.3	- 0.1
14	+ 11.3	+ 0.6	34	+ 47.0	+ 2.5
15	- 42	- 2.2			

This table shows that $|\Delta I_s|$ is less than 1.5 s. with the exception of a few anomalies corresponding to stronger divergence on $\Delta(\Delta H^{\circ}_{f_c})$ discussed in the previous section. The precision on I_s can be considered as good if we compare it with the precision generally admitted for measured specific impulse[26] which is approximately ± 1.5 s or, in relative value, ± 0.5 %.*

CONCLUSION

The method of estimation of the enthalpy of formation of molecules containing numerous NO_2 groups, described in this paper, appears as a reliable tool in the prediction of theoretical performance of non-synthetized target compounds for future high-energy solid propellants. Its precision could be improved as far as new thermochemical experimental data would be available especially for cyclic compounds. However the results obtained in its application to polynitro- or nitramine cage molecules must be considered with some caution since no experimental data have been found in the literature for comparison.

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*Measured specific impulse I_{sp} is not equal to theoretical specific impulse I_s but is lower by a quantity called "specific impulse losses", ΔI_{sl} . Still, the comparison of their uncertainties is meaningful since ΔI_{sl} can be evalutated separately, so that $|\Delta I_{sp}| \leq |\Delta I_{sl}| + |\Delta (\Delta I_{sl})|$.

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