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COMMENT/REPLY

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Comments on “Estimated Gas-Phase Standard State Enthalpies of Formation for Organic Compounds Using the Gaussian-4 (G4) and W1BD Theoretical Methods” (Rayne, S.; Forest, K. *J. Chem. Eng. Data* 2010, *55*, 5359−5364)

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In the paper of Rayne and Forest[1] a large set of gas-phase enthalpies of formation calculated by the Gaussian-4 (G4) method[2] has been reported. I would like to attract attention of the authors[1] and readers to the fact that all calculated values are overestimated. This can be seen from a comparison of the values calculated by Rayne and Forest[1] with those calculated by the authors of the G4 method[2] (Table 1). The deviations between these two calculations vary from (1.0 to 2.6) kJ·mol^{-1}. A much larger deviation is observed for the last compound in Table 1, the enthalpy of formation of which has been calculated in this work using the standard atomization energy approach.[6]

It is difficult to find a source of discrepancies between results in refs 1 and 2. The explicit expressions used by Rayne and Forest in their calculations are not given in ref 1, while the calculation scheme is represented rather schematically in the references which are cited by the authors. In this connection it would be interesting to compare the calculation scheme used in ref 1 with that commonly used in such calculations.[6−8] It is unclear why the authors[1] give the atomic enthalpies of formation at 298.15 K, while the enthalpies of formation at 0 K are used in the atomization energy calculations. In addition, the values of $H°(298)-H°(0)$ for elements in their standard states are not given in ref 1.

There is an additional reason for the large discrepancy between two G4 values for cyclopropylbenzene (Table 1). One can agree with the authors[1] that the conformational analysis of complex molecules is time-consuming process and the determination of low-energy conformations contribution to the enthalpy of formation is sometimes impractical. However, in any case, the enthalpy of formation should be calculated for the global minimum conformer. The neglect of conformational analysis could lead to large errors, and the calculation for cyclopropylbenzene provides an apt illustration. In this work the enthalpy of formation of cyclopropylbenzene was calculated for the most stable conformer (“a” in Figure 1), whereas Rayne and Forest[1] carried out their calculation for the conformer “b” which is not the global minimum conformer. As is seen from Table 1, the value calculated in this work is in much better agreement with experiment than that calculated in ref 1. It should be noted that the correction for the second stable conformer is rather small and increases the value of enthalpy of formation only by 0.7 kJ·mol^{-1}. Therefore, the enthalpies of formation of compounds presented in Tables 2 and 3 in ref 1 could be substantially overestimated if the authors[1] have not guessed the lowest energy conformer.

Table 1. Comparison of G4 and Experimental Enthalpies of Formation (kJ·mol^{-1})

	G4			deviations		
compound	(1) Rayne, Forest[a]	(2) Curtiss et al.[b]	expt.[c]	(1)−(2)	expt. −(1)	expt. −(2)[d]
CS_2	105.8	104.4	117.2	1.4	11.4	12.8
$C_4H_4N_2$ (pyrimidine)	186.8	185.4	195.8	1.4	9.0	10.4
CH_3COH	−165.3	−166.5	−166.1	1.2	−0.8	0.4
CH_3COOH	−428.8	−430.5	−432.6	1.7	−3.8	−2.1
C_3H_6 (cyclopropane)	55.2	54.2	53.1	1.0	−2.1	−1.1
CHF_3	−695.2	−696.3	−697.1	1.1	−1.9	−0.7
C_4H_4S (thiophene)	112.7	110.8	115.1	1.9	2.4	4.3
C_4H_6 (cyclobutene)	163.9	162.6	156.5	1.3	−7.4	−6.1
$(CH_3)_2SO$	−146.7	−148.5	−151.5	1.8	−4.8	−2.9
C_6H_6 (benzene)	85.6	83.4	82.4	2.2	−3.2	−1.0
C_6H_5OH (phenol)	−89.4	−91.8	−96.2	2.4	−6.8	−4.5
$C_6H_5NH_2$ (aniline)	89.7	87.7	87.0	2.0	6.8	4.5
$C_6H_5CH_3$ (toluene)	52.6	50.0	50.2	2.6	−2.4	0.2
C_5H_{12} (*n*-pentane)	−144.3	−146.0	−146.9	1.7	−2.6	−0.9
C_6H_{14} (*n*-hexane)	−165.2	−167.2	−166.9	2.0	−1.7	0.3
C_9H_{10} (cyclopropylbenzene)	160.9	154.0[e]	150.5[f]	6.9	−10.4	−3.5

[a] Ref 1. [b] The G4 values were calculated from the values of “expt.−(2)” and “expt.”; see also ref 2. [c] See ref 2 for CS_2 and pyrimidine and refs 3 and 4 for other compounds. [d] Deviations between experiment and G4 theory are given in the Supporting Information in ref 2. [e] This work. [f] Ref 5.

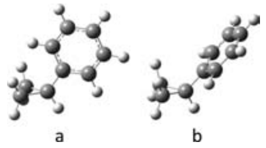

Figure 1. Two stable conformers of cyclopropylbenzene. The conformer “a” is 3.6 kJ·mol^{-1} more stable than conformer “b” by result of B3LYP/6-31G(d,p) calculations.

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