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Self-consistent enthalpies of formation of adamantanes by isodesmic reaction network

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ABSTRACT

The thermochemical network of 300 isodesmic reactions was used to simultaneously adjust the enthalpies of formation for 25 adamantanes. The experimental enthalpies of formation of these compounds were treated as unknowns in the least-squares minimization of deviations between the theoretically predicted enthalpies of reaction and experimental values. The theoretical enthalpies of reactions were obtained using Gaussian-4 (G4) method. A result of a least-squares fit confirms the accuracy of experimental enthalpies of formation of 15 adamantanes, whereas the experimental measurements for 10 adamantanes require re-examination.

1. Introduction

Adamantane and its derivatives have been of great interest in recent years due to their wide application in various fields such as nanotechnology, drug-delivery and medicine [1]. Among the properties studied are important thermochemical data: the enthalpies of formation, sublimation and combustion were determined experimentally for more than 30 adamantanes. The most thoroughly investigated of these is the unsubstituted adamantane. The experimental enthalpies of formation ($\Delta_f H_m$) of adamantane [2–6] have a scatter of 9 kJ·mol^{-1}, and at present the most reliable value is recommended by Bazyleva et al. [6] using available literature data and the authors' own results. Compared to adamantane, the enthalpies of formation of adamantane derivatives are derived from one, rarely two, experimental investigations; therefore, there is no confidence in their accuracy.

In the present work, we analyze the accuracy of available experimental data on enthalpies of formation and sublimation of adamantanes using computational chemistry methods. Adamantane and its derivatives are sufficiently large molecules for which the high-level quantum chemical calculations of enthalpy of formation, such as CCSD(T) in combination with a large basis set, require a great deal of computational resources. Because of this, the less expensive Gaussian-4 (G4) composite scheme [7] is used in this work to obtain the gas-phase enthalpies of formation. In the test sets of 38 hydrocarbons and 100 substituted hydrocarbons, enthalpies of formation predicted using G4 theory have the root-mean-square deviations from the experiment of 2.9 and 3.9 kJ·mol^{-1}, respectively. However, since there are no cage hydrocarbon compounds in this test sets, the accuracy of G4 predictions for adamantanes can be much worse. For these compounds, more reliable results can be obtained using isodesmic reactions.

Earlier the G4 method and its previous modification, G3(MP2), were used in estimating the enthalpies of formation of the adamantane derivatives [8–10]. Emel'yanenko et al. [8,9] found that theoretical enthalpies of formation calculated from the atomization procedure were systematically more negative in comparison with the experimental data. To improve the quality of predictions, the authors suggested a simple correction for theoretical values based on the correlation between the experimental and calculated values. Three isodesmic reactions with adamantane and two methyladamantanes as the reference species were used to calculate the enthalpy of formation of 5-(1-adamantyl)tetrazole [10]. A good agreement between the results of three reactions suggests that the experimental enthalpies of formation of adamantane, 1- and 2-methyladamantane are self-consistent values. None of the above works has conducted a systematic study of the consistency of all available experimental data for adamantanes.

Recently we used the G4 theory combined with isodesmic reactions to check the accuracy of various compound classes (azides, amino acids, nitro compounds, phenols, and hydrazines) [11–16]. The accuracy of these calculations was shown to be often comparable to the accuracy of the experimental data and higher-level calculations. The main emphasis in these works was on the selection of the reference species with accurate enthalpies of formations.

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Unfortunately, the choice of suitable reference species for adamantanes is limited because of their cage structure. Obviously, in this case the best results will be obtained if the adamantanes themselves are used as model compounds, and so the knowledge of the accuracy of their $\Delta_f H_m(g)$ values becomes paramount.

In this work, an isodesmic reaction network based on 25 experimental determinations was created to check the accuracy and internal consistency of experimental enthalpies of formation of adamantanes. The network involves the $\Delta_f H_m(g)$ values for compounds **1**–**25** (Table 1) extracted from the literature and contains 300 reactions involving these compounds. The enthalpies of formation of 25 adamantanes were determined by simultaneous least-squares adjustment of experimentally based enthalpies of formation to minimize the discrepancy between the calculated and experimental enthalpies of isodesmic reactions. The use of thermochemical network approach in Active Thermochemical Tables (ATcT) provides reliable, accurate, and internally consistent enthalpies of formation for a broad range of chemical species [36–38]. Also, the theoretical enthalpies of isodesmic reactions, together with experimental data, are used to check the consistency of available experimental data for different group of compounds [39–42].

Table 1
Experimental and theoretical enthalpies of formation in both condensed and gaseous phases and enthalpies of sublimation of adamantane and its derivatives.[a]

	Compound	Experiment				Calculation (G4)	
		$\Delta_f H_m$(cr)/kJ·mol^{-1}	$\Delta^g_{cr} H_m$/kJ·mol^{-1}	$\Delta_f H_m$(g)/ kJ·mol^{-1}	Reference	$\Delta_f H_m$(g)/kJ·mol^{-1} Atomization reaction	$\Delta_f H_m$(g)/kJ·mol^{-1}Isodesmic reaction network
1	Adamantane	−197.2 ± 0.8	59.3 ± 0.2	−137.9 ± 0.8	[2]	−139.3	−132.0
		−188.4 ± 3.3			[3]		
		−188.7 ± 2.8	60.5 ± 1.3	−128.2 ± 4.1	[4]		
		−192.5 ± 0.3	59.7 ± 0.8 (323 K)	−132.9 ± 1.3	[5]		
		−193.3 ± 0.3[b]	59.4 ± 0.2[b]	−133.9 ± 0.4	[17]		
		−191.6 ± 3.0			[6]		
		−189.5 ± 3.2			[6]		
		−191.4 ± 2.0[b]	59.1 ± 0.9	**−132.3 ± 2.2**	[6]		
2	1-Methyladamantane	−242.7 ± 1.7	67.8 ± 1.3	**−174.9 ± 2.1**	[18]	−183.1	−175.3
		−237.3 ± 1.3	67.6 ± 0.5	−169.7 ± 1.4	[5]		
		−239.3 ± 2.5	67.7	−171.6 ± 2.7[c]	[19]		
3	2-Methyladamantane	−224.7 ± 1.7	68.2 ± 1.3	**−156.5 ± 2.1**	[18]	−166.6	−158.9
		−216.7 ± 1.2	67.5 ± 2.1 (320 K)	−149.2 ± 2.6	[5]		
		−219.6 ± 3.8	67.9	−151.7 ± 4.1	[19]		
4	1,3-Dimethyladamantane	−286.6 ± 2.5	67.8 ± 1.3	**−218.8 ± 2.9**	[18]	−224.6	−217.5
				−213.0 ± 2.3[d]	[20]		
5	2,2-Dimethyladamantane	−256.4 ± 2.5	73.6 ± 1.3	**−182.8 ± 2.9**	[18]	−191.1	−184.1
6	1-Ethyladamantane			**−190.4 ± 3.0**[d]	[20]	−198.7	−191.6
7	1,3,5-Trimethyladamantane	−332.6 ± 4.2	77.8 ± 1.3	−254.8 ± 4.2	[18]	−269.1	−261.8
				−255.5 ± 2.7	[20]		
				−261.8 ± 3.0	This work		
8	1,3,5,7-Ttetramethyladamantane	−378.7 ± 3.8	83.7 ± 1.3	**−295.0 ± 3.8**	[18]	−305.4	−297.6
		−362.1 ± 2.0	81.1 ± 0.9	−281.0 ± 2.1	[5]		
		−365.8 ± 6.8	82.4	−283.4 ± 6.9[c]	[19]		
9	1-Adamantanol	−397.5 ± 2.5	86.6 ± 2.5	−310.9 ± 3.3	[21]	−326.0	−316.9
		−389.1 ± 2.0	82.0 ± 1.5	−307.1 ± 2.5	[17]		
			86.73 ± 0.22		[22]		
		−403.0 ± 2.2			[9]		
		−401.5 ± 2.0[b]	86.6 ± 0.6[b]	**−314.9 ± 2.1**	[9]		
10	2-Adamantanol	−387.9 ± 3.8	88.7 ± 2.5	**−299.2 ± 4.6**	[21]	−310.3	−301.3
			88.14 ± 1.60		[22]		
11	2-Adamantanone	−310.9 ± 3.8	80.3 ± 2.5	−230.5 ± 4.6	[21]	−246.6	−236.3
		−319.7 ± 1.2	76.1 ± 1.5	−243.6 ± 1.9	[17]		
			66.38 ± 0.25		[23]		
		−306.8 ± 2.5	66.0 ± 0.4		[9]		
		−307.5 ± 1.4[b]	65.8 ± 0.6[b]	−241.7 ± 1.5	[9]		
				−236.3 ± 3.0	This work		
12	1-Acetyladamantane	−382.5 ± 3.1	84.2 ± 0.6	**−298.3 ± 3.2**	[24]	−307.4	−298.7
			84.9 ± 0.6		[9]		
13	1-Adamantanecarboxylic acid	−643.1 ± 3.8			[25]	−523.2	−516.3
		−643.1 ± 3.8[e]	98.7 ± 4.5	−544.4 ± 5.9	[26]		
			98.3 ± 1.8		[9]		
		−614.6 ± 5.0[f]		**−516.3 ± 3.0**	This work		
14	2-Adamantanecarboxylic acid	−627.2 ± 3.8			[25]	−516.8	−509.8
		−627.2 ± 3.8[e]	99.8 ± 1.8	−527.4	[9]		
		−609.6 ± 5.0[f]		**−509.8 ± 3.0**	This work		
15	1-Carbomethoxyadamantane	−577.8 ± 2.6	82.4 ± 0.6	**−495.4 ± 2.7**	[27]	−504.9	−494.3
16	1-Aminoadamantane	−195.4 ± 2.3	61.7 ± 0.63	−133.8 ± 2.4	[28]	−136.1	−128.9
				−128.9 ± 3.0	This work		
17	1-Cyanoadamantane	−83.5 ± 1.8	76.0 ± 1.1	−7.5 ± 2.1	[29]	−20.5	−10.8
		−88.3 ± 2.5	67.3 ± 0.8	−21.0 ± 2.6	[27]		
		−86.7 ± 2.1[b]	77.0 ± 1.2[g]	**−9.7 ± 2.4**	[8]		
18	2-Cyanoadamantane	−83.1 ± 2.0	75.8 ± 1.1	**−7.3 ± 2.3**	[8]	−16.3	−6.7
19	1-Adamantylcarboxamide	−427.0 ± 2.4	108.0 ± 0.5	**−319.0 ± 2.5**	[30]	−327.6	−319.8
20	*N*,*N*-Dimethyl-1-adamantylcarboxamide	−383.6 ± 2.7	97.5 ± 0.3	−286.1 ± 2.7	[31]	−299.4	−290.7
				−290.7 ± 3.0	This work		