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Article

Thermochemistry of Furan and Its Derivatives: A High-Level Ab Initio Study

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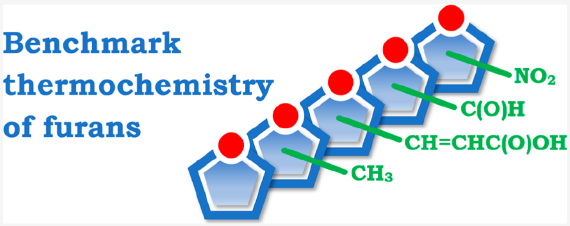
ABSTRACT: The standard molar enthalpies of formation in the gas phase at $T = 298.15$ K for 43 furan derivatives were calculated using the DLPNO−CCSD(T$_1$)/CBS method in conjunction with isodesmic-type reactions to assess the accuracy of experimental data reported in the literature. The high accuracy of the experimental data was confirmed for almost half of the studied compounds (44%). For the remaining furans, the discrepancy between the experimental and theoretical values is larger than 5−70 kJ·mol^{-1}, and additional experimental measurements are obviously required to determine more accurate values of the enthalpy of combustion and/or enthalpy of phase change. The experimental enthalpies of formation of 12 furans are recommended as benchmark reference values for use in thermochemical calculations of furan-based compounds.



INTRODUCTION

The conversion of biomass into fuels and chemicals is considered to be the source of carbohydrate feedstocks that can be used as a renewable alternative to petroleum-based resources. Among the biomass-derived molecules, the derivatives of furan play an important role. Furfural and 5-hydroxymethylfurfural are the most common biofurans formed in the dehydration of lignocellulosic biomass. These promising biofurans can be further converted into a variety of chemicals (furfuryl alcohol, 2,5-dimethylfuran, 2,5-diformylfuran, 2,5-furandicarboxylic acid, 2,5-bis(hydroxymethyl)furan, 2,5-bis(aminomethyl)furan, 5-ethoxymethylfurfural, tetrahydrofuran, 2-methyltetrahydrofuran, and other derivatives of furan as well as levulinic acid, maleic anhydride, γ-valerolactone, succinic acid etc.) which are widely used in various industries.[1−4]

There is growing interest in the use of furans as transportation fuels. The studies of physical, chemical, mechanical, and environmental characteristics and ignition behavior of furan derivatives have shown that they possess favorable combustion properties to be used as pure fuels or fuel additives.[5−8] Modeling the combustion properties and chemical kinetic modeling are of great importance in characterizing the performance of furanic fuels. The thermochemical properties such as enthalpies of formation and vaporization are necessary in these theoretical studies.[9−11] Another attractive field of application of biomass-derived furan compounds is their use as promising liquid organic hydrogen carriers (LOHCs) for hydrogen storage.[12−14] In this case, the knowledge of thermochemical characteristics helps to choose suitable LOHC compounds.

The experimental values of the enthalpy of formation ($\Delta_f H^\circ_{298}$) in the condensed phase and enthalpy of vaporization ($\Delta_{vap} H^\circ_{298}$) or sublimation ($\Delta_{sub} H^\circ_{298}$) have been determined for more than 40 furan derivatives. The accuracy of the reported experimental data can be assessed by comparing the experimental $\Delta_f H^\circ_{298}(g)$ values ($\Delta_f H^\circ_{298}(g) = \Delta_f H^\circ_{298}(l) + \Delta_{vap} H^\circ_{298}$ or $\Delta_f H^\circ_{298}(g) = \Delta_f H^\circ_{298}(cr) + \Delta_{sub} H^\circ_{298}$) with those calculated using the quantum-chemical methods. Several such calculations have been published previously.[11,15−20] In these studies, the theoretical enthalpies of formation were reported for less than half of the compounds with the available experimental data. For most of the compounds, the calculations were performed using the composite CBS-QB3, CBS-APNO, G3, and G4 methods,[11,18−20] which at that time were still the most commonly used in computational thermochemistry.

In this study, the domain localized pair natural orbital coupled cluster method with improved iterative triples, DLPNO−CCSD(T$_1$),[21−23] was used in conjunction with isodesmic-type reactions[24] to assess the accuracy of experimental data for 43 furan derivatives. Although this method was developed fairly recently, it is now quite widely used for accurate prediction of gas-phase enthalpies of formation.[17,25−29] In our previous works,[28−32] we have shown the advantage of this method in comparison with the composite G4 method, which is especially pronounced for cyclic compounds. The purpose of this study was also to determine a set of furan compounds whose experimental gas-phase

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enthalpies of formation can be used as benchmark values in thermochemical calculations based on the isodesmic reaction approach.

COMPUTATIONAL DETAILS

Geometry Optimization and Calculation of Vibrational Frequencies. The geometries and harmonic vibrational frequencies of furan derivatives and all compounds used in isodesmic-type reactions were calculated at the B3LYP-D3(BJ)/def2-TZVPP level of theory. Geometry optimizations were performed with the "Tight" option using the Gaussian 16 suite of programs.[33] The conformational analysis was preliminarily performed for flexible molecules. For molecules with one or two internal rotations, the one-dimensional potential energy profiles were calculated for each internal rotation degree of freedom. The minima were located by inspection of the calculated torsional profiles, unconstrained optimizations, and frequency calculations. A search of low-energy conformers of more flexible molecules was performed with MMFF94 force field using GMMX conformational searching methodology implemented in GaussView 6.[34] The resulting conformers were further optimized at the B3LYP-D3(BJ)/def2-TZVPP density functional theory level. The most stable conformers were used to calculate the enthalpies of isodesmic-type reactions; their Cartesian coordinates are given in Table S1.

Although some of the furans used in this study are conformationally flexible molecules, the conformer contribution to the enthalpy of formation was neglected. In many cases, the products in the working reactions are conformationally similar to the reagent structures, and this leads to the cancellation of errors associated with the conformational flexibility. Moreover, it has been shown that the conformer correction is partially compensated by the neglect of anharmonicity of low-frequency torsional motions used in the calculation of vibrational zero-point energies (ZPEs) and enthalpic corrections.[35,36]

The ZPEs and enthalpic corrections ($H^\circ_{298} - H^\circ_0$) were estimated within the rigid rotor−harmonic oscillator approximation using the computed frequencies scaled with the factor of 0.9883 recommended for the prediction of ZPEs calculated by the B3LYP/def2-TZVPP model.[37]

Single-Point Energy Calculations. The total electronic energies (E_e) necessary for the accurate evaluation of enthalpies of reaction were calculated using the DLPNO−CCSD(T$_1$) method.[21−23] The single-point DLPNO−CCSD(T$_1$)/CBS//B3LYP-D3(BJ)/def2-TZVPP energies were obtained using "TightSCF" and "TightPNO" settings at the extrapolated complete basis set (CBS) limit using cc-pVTZ and cc-pVQZ basis sets. The ORCA 5.0.3 program release[38−40] was employed for these calculations, including the extrapolation procedure implemented in ORCA. The DLPNO−CCSD(T$_1$)/CBS energies corrected for the ZPE and for the change in enthalpy on going from 0 to 298 K ($H^\circ_{298} - H^\circ_0$) were used to calculate the enthalpies of isodesmic-type reactions. The total electronic energies together with the ZPE and enthalpic corrections are summarized in Table S2.

Working Reactions and Reference Species. The isodesmic-type reactions[24] with different reference species and the same number of molecules on both sides of the equation were used in the present calculations taking into account previously obtained results for different organic molecules.[28−32] The accurate $\Delta_f H^\circ_{298}$(g) values for small reference molecules were taken from the Active Thermochemical Tables (ATcT).[41,42] For several reference molecules (*tert*-butylbenzene, tetrahydrofuran, tetrahydrofurfuryl alcohol, benzaldehyde, benzoic acid, nitromethane, nitrobenzene, 2-butanone oxime, and cyclohexanone oxime), the experimental data from the original papers were used; their accuracy was confirmed by preliminary quantum-chemical calculations. In addition to these reference species, furan and 11 of its derivatives were also used in isodesmic reactions. As shown in our study (see below), the experimental data for these compounds might be considered of benchmark quality.

Table 1 compares the enthalpy of formation of furan calculated using only the reference molecules taken from ATcT[41] (reactions 1−4) with the value obtained using furan derivatives (reactions 5−11). As can be seen, the results of these two calculations agree well with each other, supporting the use of furan derivatives for the calculation of benchmark thermochemical data. It should be noted that even the hydrogenation reaction gives good agreement with the experimental result. Usually, these reactions lead to increased deviations from the experimental values and are therefore not used in the calculations. The G4 method,[43] widely used in thermochemical calculations, gives a value of −38.6 kJ·mol^{-1} for reaction 1, while a value of −33.6 kJ·mol^{-1}, which is close to the experimental one (−34.7 kJ·mol^{-1}), is obtained for reaction 3. To see what results the hydrogenation reaction produces for furan derivatives, this reaction is given in Table S3 after the working reactions used to calculate the enthalpies of formation.

Table 1. Standard Molar Enthalpy of Formation of Furan (C_4H_4O (1)) in the Gas Phase at 298.15 K Calculated Using Different Isodesmic-Type Reactions (in kJ·mol^{-1})

	reaction	$\Delta_f H^\circ_{298}$	Δ[a]
	Isogyric Reactions Involving Only Small Reference Compounds from ATcT		
1	C_4H_4O (**1**) + $2H_2 \rightarrow H_2O + C_2H_4 + C_2H_2$	−34.1	−0.6
2	C_4H_4O (**1**) + $4CH_4 \rightarrow 3C_2H_4 + C_2H_6 + H_2O$	−33.8	−0.9
3	C_4H_4O (**1**) + $3CH_4 \rightarrow 3C_2H_4 + CH_3OH$	−33.2	−1.5
4	C_4H_4O (**1**) + $C_2H_6 \rightarrow C_5H_6$ (cyclopentadiene) + CH_3OH	−33.0	−1.7
	weighted average:	−33.5 ± 1.6	−1.2
	Reactions Involving Furan Derivatives[b]		
5	C_4H_4O (**1**) + $C_2H_6 \rightarrow C_5H_6O$ (**2**) + CH_4	−34.7	0.0
6	C_4H_4O (**1**) + C_2H_6 + HC(O)H → $C_5H_4O_2$ (**7**) + $2CH_4$	−33.8	−0.9
7	C_4H_4O (**1**) + $CH_3C(O)H + C_2H_6 \rightarrow C_6H_6O_2$ (**9**) + $2CH_4$	−33.5	−1.2
8	C_4H_4O (**1**) + $CH_3C(O)H + CH_3OH + C_2H_6 \rightarrow C_6H_6O_3$ (**11**) + $3CH_4$	−33.1	−1.6
9	C_4H_4O (**1**) + $CH_3C(O)CH_3 \rightarrow C_6H_6O_2$ (**15**) + CH_4	−35.5	0.8
10	C_4H_4O (**1**) + $CH_3C(O)OH + C_2H_4 + C_2H_6 \rightarrow C_7H_6O_3$ (**20**) + $3CH_4$	−32.0	−2.7
11	C_4H_4O (**1**) + $CH_3NO_2 \rightarrow C_4H_3NO_3$ (**29**) + CH_4	−34.4	−0.3
	weighted average:	−33.8 ± 2.8	−0.9

[a] Difference between the experimental $\Delta_f H^\circ_{298}$ value (−34.7 ± 0.6 kJ·mol^{-1})[44,45] and that calculated from isodesmic-type reaction. [b] The numbers in parentheses correspond to the numbering of compounds in Table 2: **1** is furan, **2** is 2-methylfuran, **7** is furfural, **9** is 5-methylfurfural, **11** is 5-hydroxymethylfurfural, **15** is 2-acetylfuran, **20** is 2-furanacrylic acid, and **29** is 2-nitrofuran.

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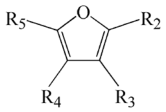
Table 2. Standard Molar Enthalpies of Formation ($\Delta_f H^\circ_{298}$) in Both Condensed and Gaseous Phases and Enthalpies of Vaporization ($\Delta_{vap} H^\circ_{298}$) or Sublimation ($\Delta_{sub} H^\circ_{298}$) at T = 298.15 K of Furan Derivatives (in kJ·mol^{-1})



			experiment				calculation[c]	
	compound[a]	substituents[b]	$\Delta_f H^\circ_{298}$(l) or $\Delta_f H^\circ_{298}$(cr)	$\Delta_{vap} H^\circ_{298}$ or $\Delta_{sub} H^\circ_{298}$	$\Delta_f H^\circ_{298}$(g)	ref(s)	$\Delta_f H^\circ_{298}$(g)	Δ[d]
1	furan (l), C_4H_4O, 110-00-9		−62.4 ± 0.6	27.7 ± 0.1	−34.7 ± 0.6	44, 45	−34.3 ± 2.0	−0.4
							−31.2[e]	
							−34.8 ± 3.0[f]	
							−31.4[g]	
							−34.9[h]	
2	2-methylfuran (l), C_5H_6O, 534-22-5	R_2 = CH_3	−108.3 ± 1.1	31.9 ± 0.5	−76.4 ± 1.2	46	−76.0 ± 2.0	−0.4
							−80.3 ± 5.0[f]	
							−75.3[g]	
3	2,5-dimethylfuran (l), C_6H_8O, 625-86-5	R_2 = R_5 = CH_3	−159.9 ± 1.0	31.8 ± 0.3	−128.1 ± 1.0	47	−117.6 ± 2.6	−10.5
							−124.6 ± 6.0[f]	
							−117.3[h]	
4	2-*tert*-butylfuran (l), $C_8H_{12}O$, 7040-43-9	R_2 = $C(CH_3)_3$	−201.9 ± 0.7	38.1 ± 0.4	−163.8 ± 0.8	47	−156.6 ± 6.6	−7.2
5	2,5-di-*tert*-butylfuran (l), $C_{12}H_{20}O$, 4789-40-6	R_2 = R_5 = $C(CH_3)_3$	−350.0 ± 0.8	56.1 ± 1.1	−293.9 ± 1.4	47	−278.5 ± 6.8	−15.4
6	furfuryl alcohol (l), $C_5H_6O_2$, 98-00-0	R_2 = CH_2OH	−280.9 ± 1.1	59.3 ± 0.4	−221.6 ± 1.2	12	−217.9 ± 3.3	−3.7
			−276.4			48	−219.3[h]	
							−220.0 ± 1.7[i]	
7	furfural (l), $C_5H_4O_2$, 98-01-1	R_2 = C(O)H	−201.7 ± 4.6	50.6 ± 0.4	−151.0 ± 5.0	44	−152.0 ± 2.4	1.0
				50.7 ± 0.2		49	−152.8[h]	
							−157.2 ± 1.6[i]	
8	3-furaldehyde (l), $C_5H_4O_2$, 498-60-2	R_3 = C(O)H	−200.0 ± 1.0	48.1 ± 0.5	−151.9 ± 1.1	50	−150.0 ± 2.6	−1.9
							−152.1[h]	
							−153.9 ± 1.4[i]	
9	5-methylfurfural (l), $C_6H_6O_2$, 620-02-0	R_2 = C(O)H, R_5 = CH_3	−252.6 ± 1.4	55.8 ± 1.2	−196.8 ± 1.8	46	−196.6 ± 2.4	−0.2
				49.7 (373 K)		51	−204.2 ± 1.4[i]	
10	4,5-dimethylfurfural (l), $C_7H_8O_2$, 52480-43-0	R_2 = C(O)H, R_4 = R_5 = CH_3	−294.5 ± 1.7	57.7 ± 0.6	−236.8 ± 1.8	52	−228.3 ± 2.4	−8.5
							−238.3 ± 2.2[i]	
11	5-hydroxymethylfurfural (cr), $C_6H_6O_3$, 67-47-0	R_2 = C(O)H, R_5 = CH_2OH	−437.4 ± 1.3	103.2 ± 0.5	−334.2 ± 1.4	53	−334.5 ± 2.4	0.3
							−342.5 ± 3.0[i]	
12	2-furancarboxylic acid (cr), $C_5H_4O_3$, 88-14-2	R_2 = C(O)OH	−498.5 ± 1.4	88.2 ± 1.5	−410.3 ± 2.1	54	−405.4 ± 4.8	−4.9
			−503.7 ± 1.3	92.8 ± 2.3	−410.9 ± 2.6	55	−412.1 ± 1.7[i]	
			−498.4			48		
				87.1 ± 0.8		56		
				88.6 ± 0.8		56		
13	3-furancarboxylic acid (cr), $C_5H_4O_3$, 488-93-7	R_3 = C(O)OH	−502.4 ± 1.6	86.6 ± 0.5	−415.8 ± 1.7	54	−410.8 ± 4.2	−5.0
							−415.5 ± 1.8[i]	

Table 2. continued

			experiment				calculation[c]	
	compound[a]	substituents[b]	$\Delta_f H^\circ_{298}(l)$ or $\Delta_f H^\circ_{298}(cr)$	$\Delta_{vap} H^\circ_{298}$ or $\Delta_{sub} H^\circ_{298}$	$\Delta_f H^\circ_{298}(g)$	ref(s)	$\Delta_f H^\circ_{298}(g)$	Δ[d]
14	2,5-dimethyl-3-furancarboxylic acid (cr), $C_7H_8O_3$, 636-44-2	$R_2 = R_5 = CH_3$, $R_3 = C(O)OH$	−600.4 ± 1.5	100.9 ± 0.5	−499.5 ± 1.6	52	501.2 ± 4.8	1.7
							−509.6 ± 2.5[i]	
15	2-acetylfuran (l), $C_6H_6O_2$, 1192-62-7	$R_2 = C(O)CH_3$	−260.4 ± 1.2	53.0 ± 0.6	−207.4 ± 1.3	50	−204.9 ± 3.6	−2.5
							−205.0[h]	
							−210.3 ± 1.8[i]	
16	5-methyl-2-acetylfuran (l), $C_7H_8O_2$, 1193-79-9	$R_2 = C(O)CH_3$, $R_5 = CH_3$	−311.3 ± 1.4	57.4 ± 1.3	−253.9 ± 1.9	46	−249.5 ± 3.5	−4.4
							−257.0 ± 2.0[i]	
17	2,5-dimethyl-3-acetylfuran (l), $C_8H_{10}O_2$, 10599-70-9	$R_2 = R_5 = CH_3$, $R_3 = C(O)CH_3$	−352.1 ± 1.8	57.5 ± 1.5	−294.6 ± 2.3	52	−288.4 ± 2.7	−6.2
							−297.6 ± 2.1[i]	
18	methyl 2-furancarboxylate (l), $C_6H_6O_3$, 611-13-2	$R_2 = C(O)OCH_3$	−450.2 ± 0.4	45.2 ± 0.8	−405.0 ± 2.1	57	−383.3 ± 1.4	−21.7
19	2-furanacrolein (cr), $C_7H_6O_2$, 623-30-3	$R_2 = CH{=}CHC(O)H$	−186.3 ± 1.5	82.3 ± 0.4	−104.0 ± 1.6	58	−101.0 ± 3.0	−3.0
			−182.0 ± 0.8	76.1 ± 2.1	−105.9 ± 2.5	57		
20	2-furanacrylic acid (cr), $C_7H_6O_3$, 539-47-9	$R_2 = CH{=}CHC(O)OH$	−462.3 ± 1.0	103.3 ± 0.5	−359.0 ± 1.1	58	−358.8 ± 4.6	−0.2
			−419.6 ± 2.6	104.3 ± 4.7	−315.3 ± 5.2	55		
21	3-furanacrylic acid (cr), $C_7H_6O_3$, 39244-10-5	$R_3 = CH{=}CHC(O)OH$	−460.6 ± 1.2	106.8 ± 0.5	−353.8 ± 1.3	58	−348.9 ± 4.6	−4.9
22	2-(diacetoxymethyl)furan (cr), $C_9H_{10}O_5$, 613-75-2	$R_2 = CH[OC(O)CH_3]_2$	−882.4 ± 0.4	109.6 ± 2.5	−772.8 ± 2.5	57	−786.1 ± 5.9	13.3
23	furfurylamine (l), C_5H_7NO, 617-89-0	$R_2 = CH_2NH_2$	−105.4 ± 8.6	67.1[j]		59	−38.3 ± 2.2	
24	2-furancarbonitrile (l), C_5H_3NO, 617-90-3	$R_2 = CN$	62.0 ± 1.0	44.8 ± 0.4	106.8 ± 1.1	50	110.7 ± 1.3	−3.9
25	2-furanacrylonitrile, mixture (l), C_7H_5NO, 7187-01-1	$R_2 = CH{=}CHCN$	93.4 ± 1.6	65.2 ± 0.6	158.6 ± 1.7	58	151.9 ± 2.4	6.7
26	ethyl-2-cyano-3-(furan-2-yl)prop- 2-enoate (cr), $C_{10}H_9NO_3$, 23973-22-0	$R_2 = CH{=}C(CN)C(O)OCH_3$	−331.9 ± 6.5	102.9 ± 5.6	−230.0 ± 8.5	60	−230.8 ± 4.3	0.8
27	ethyl 2-cyano-3-(5-phenyl-2-furanyl)-2-propenoate (cr), $C_{16}H_{13}NO_3$, 155106-29-9	$R_2 = CH{=}C(CN)C(O)OCH_3$, $R_5 = C_6H_5$	−253.2 ± 2.7	139.8 ± 7.0	−113.4 ± 8.5	60	−149.0 ± 4.6	35.6
28	ethyl 2-cyano-3-[5-(4-methylphenyl)-2-furanyl]-2-propenoate (cr), $C_{17}H_{15}NO_3$, 304896-34-2	$R_2 = CH{=}C(CN)C(O)OCH_3$, $R_5 = C_6H_4CH_3$	−297.9 ± 2.7	148.9 ± 8.2	−149.0 ± 8.5	60	−181.4 ± 4.0	32.4
29	2-nitrofuran (cr), $C_4H_3NO_3$, 609-39-2	$R_2 = NO_2$	−104.2 ± 0.4	75.3 ± 2.1	−28.9 ± 2.5	57	−27.4 ± 3.7	−1.5
							−31.2 ± 4.0[k]	
30	5-nitrofurfural (cr), $C_5H_3NO_4$, 698-63-5	$R_2 = C(O)H$, $R_5 = NO_2$	−226.8 ± 0.4	79.5 ± 2.5	−147.3 ± 2.5	57	−137.8 ± 4.1	−9.5
31	5-(2-nitrophenyl)furfural (cr), $C_{11}H_7NO_4$, 20000-96-8	$R_2 = C(O)H$, $R_5 = C_6H_4$-*o*-NO_2	−193.9 ± 6.8	107.8 ± 6.7	−86.1 ± 9.7	61	−57.0 ± 2.3	−29.1
32	5-(3-nitrophenyl)furfural (cr), $C_{11}H_7NO_4$, 13148-43-1	$R_2 = C(O)H$, $R_5 = C_6H_4$-*m*-NO_2	−203.5 ± 8.0	132.5 ± 3.9	−71.0 ± 8.9	61	−80.0 ± 2.3	9.0
33	5-(4-nitrophenyl)furfural (cr), $C_{11}H_7NO_4$, 7147-77-5	$R_2 = C(O)H$, $R_5 = C_6H_4$-*p*-NO_2	−224.5 ± 6.7	135.9 ± 3.5	−88.6 ± 7.6	61	−80.1 ± 2.3	−8.5
			−224.4 ± 4.4			62		
34	3-[5-(2-nitrophenyl)-2-furyl]acrylic acid (cr), $C_{13}H_9NO_5$, 58110-36-4	$R_2 = CH{=}CHC(O)OH$, $R_5 = C_6H_4$-*o*-NO_2	−398.7 ± 5.3	203.9 ± 2.3	−194.8 ± 5.8	63	−266.3 ± 5.4	71.5
35	3-[5-(3-nitrophenyl)-2-furyl]acrylic acid (cr), $C_{13}H_9NO_5$, 58110-35-3	$R_2 = CH{=}CHC(O)OH$, $R_5 = C_6H_4$-*m*-NO_2	−412.9 ± 5.7	185.4 ± 6.5	−227.5 ± 8.6	63	−289.3 ± 5.4	61.8
36	3-[5-(4-nitrophenyl)-2-furyl]acrylic acid (cr), $C_{13}H_9NO_5$, 58110-34-2	$R_2 = CH{=}CHC(O)OH$, $R_5 = C_6H_4$-*p*-NO_2	−431.3 ± 6.8	206.7 ± 5.6	−224.6 ± 8.8	63	−289.9 ± 5.4	65.3
37	5-(2-nitrophenyl)furfural oxime (cr), $C_{11}H_8N_2O_4$, 22649-16-7	$R_2 = CH{=}NOH$, $R_5 = C_6H_4$-*o*-NO_2	−13.1 ± 4.0	148.4 ± 7.5	135.3 ± 8.5	63	83.8 ± 3.7	51.5
38	5-(3-nitrophenyl)furfural oxime (cr), $C_{11}H_8N_2O_4$, 13130-07-9	$R_2 = CH{=}NOH$, $R_5 = C_6H_4$-*m*-NO_2	−29.9 ± 3.6	137.2 ± 3.9	107.3 ± 5.3	63	60.3 ± 3.7	47.0

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Table 2. continued

			experiment				calculation[c]	
	compound[a]	substituents[b]	$\Delta_fH^\circ_{298}(l)$ or $\Delta_fH^\circ_{298}(cr)$	$\Delta_{vap}H^\circ_{298}$ or $\Delta_{sub}H^\circ_{298}$	$\Delta_fH^\circ_{298}(g)$	ref(s)	$\Delta_fH^\circ_{298}(g)$	Δ[d]
39	5-(4-nitrophenyl)furfural oxime (cr), $C_{11}H_8N_2O_4$, 19934-32-8	R_2 = CH═NOH, R_5 = C_6H_4-*p*-NO_2	−49.7 ± 5.2	157.7 ± 2.7	108.0 ± 5.9	63	59.5 ± 3.7	48.5
40	methyl 5-nitro-2-furancarboxylate (cr), $C_6H_5NO_5$, 1874-23-3	R_2 = C(O)OCH_3, R_5 = NO_2	−471.1 ± 0.4	104.2 ± 2.1	−366.9 ± 2.1	57	−373.2 ± 4.2	6.3
41	2-(diacetoxymethyl)-5-nitrofuran (cr), $C_9H_9NO_7$, 92-55-7	R_2 = CH[OC(O)CH_3]$_2$, R_5 = NO_2	−897.9 ± 0.8	126.4 ± 2.5	−771.5 ± 2.5	57	−779.5 ± 7.5	8.0
42	5-nitro-2-furanacrolein (cr), $C_7H_5NO_4$, 1874-22-2	R_2 = CH═CHC(O)H, R_5 = NO_2	−162.8 ± 1.3	97.9 ± 2.1	−64.9 ± 2.5	57	−90.1 ± 4.1	25.2
43	2-furancarboxylic acid hydrazide (cr), $C_5H_6N_2O_2$, 3326-71-4	R_2 = C(O)NHNH2	−205.5 ± 0.9	99 ± 0.7	−106.5 ± 1.1	64	−106.1 ± 3.7 −108.0 ± 2.0[l]	−0.4

[a] The CAS Registry Numbers are given after the molecular formulas; the IUPAC names of compounds are given in Table S3. [b] The substituents R_2−R_5 are indicated when they differ from the H atom. The drawings of chemical structures are given in Table S3. [c] The weighted average value calculated in this work is given first; its approximate uncertainty was computed as described in the text. [d] Difference between the first experimental $\Delta_fH^\circ_{298}(g)$ value and that calculated in this work. [e] CCSD(T)/CBS calculation taking into account the zero-point vibrational energy, core−valence, and scalar relativistic corrections, atomization reaction, ref 15. [f] CCSD(T)-F12b/cc-pVQZ-F12 calculations, atomization reaction, ref 16. [g] CBS-QB3 and CBS-APNO calculations using isodesmic reactions, ref 18. [h] Atom equivalents approach based on the DLPNO−CCSD(T)/def2-QZVP//B3LYP-D3(BJ)/def2-TZVP calculations, ref 17. [i] CBS-QB3, CBS-APNO, and G3 calculations using isodesmic reactions, ref 11. [j] This value is equal to the difference between $\Delta_fH^\circ_{298}(g)$ and $\Delta_fH^\circ_{298}(l)$; it is estimated as the sum of the vaporization enthalpy and the dissociation enthalpy of dimer (see ref 59 for details). [k] G4 calculations using isodesmic reactions, ref 19. [l] G4 calculations using isodesmic reactions, ref 20.

Uncertainty of Calculated Values. The overall uncertainty of the $\Delta_fH^\circ_{298}(g)$ values obtained from quantum-chemical calculations is a combination of uncertainties from the calculated enthalpies of working reactions ($\Delta_rH^\circ_{298}$) and the enthalpies of formation of the reference molecules involved in these reactions. In this study, the approximate uncertainty of the calculated enthalpies of formation was determined in the following way. The uncertainty associated with each working reaction was estimated as a combined standard uncertainty of the experimental enthalpies of formation of the reference molecules and of the calculated value of the enthalpy of reaction; the last uncertainty was estimated as 4 kJ·mol^{-1}. Using these data, the weighted average $\Delta_fH^\circ_{298}(g)$ values were calculated, and they are given in Tables 1 and 2. The uncertainties of these values were defined as $s_d \times t$, where s_d is the standard deviation from the weighted average value and t is Student's coefficient for the 95% confidence level.

RESULTS AND DISCUSSION

Furan. Knowing the exact value of the gas-phase enthalpy of formation of furan is important not only for checking the accuracy of published experimental data but also for its use in calculating the enthalpies of formation of various furan derivatives by the method of isodesmic reactions. The combustion energy and vapor pressure measurements were made for furan by Guthrie et al.[45] in 1952, and their experimental values of enthalpy of formation and vaporization (Table 2) have been recommended in the well-known book by Cox and Pilcher[44] based on the experimental quality of the reported work. No other experimental thermochemical studies of furan have been reported, and therefore, the comparison with high-level quantum-chemical calculations is of particular interest.

As can be seen in Table 2, along with our value, two calculated values[16,17] agree well with the experimental $\Delta_fH^\circ_{298}(g)$ value of −34.7 kJ·mol^{-1}; these values were determined using the CCSD(T)-F12b and DLPNO−CCSD(T) methods. Two other values (−31.4 and −31.2 kJ·mol^{-1})[18,15] are about 3.5 kJ·mol^{-1} larger than the experimental one. The first value was obtained from the CBS-QB3 and CBS-APNO calculations, and the deviation from the experimental value is within the accuracy of these models. The second value was calculated using the CCSD(T)/CBS method including core−valence and scalar relativistic corrections, and its accuracy is expected to be high. However, the enthalpies of formation of cyclopentadiene and pyrrole calculated by the same method (136.8 and 110.9 kJ·mol^{-1})[15] also are larger than the experimental values (134.3 ± 0.6 and 108.3 ± 0.5 kJ·mol^{-1}),[41,44] which does not allow us to consider these calculations as sufficiently accurate.

Thus, the most reliable theoretical calculations of the enthalpy of formation of furan show good agreement with the experimental $\Delta_fH^\circ_{298}(g)$ value, which can be considered to be of benchmark quality. Together with small reference molecules from ATcT,[41] furan was used in this study as a reference species to estimate the enthalpies of formation of all furan derivatives.

Furans with |$\Delta_fH^\circ_{298}$(g, exp) − $\Delta_fH^\circ_{298}$(g, calc)| Values Less than or Equal to 2.5 kJ·mol^{-1}. The results of the present calculations are given in Table 2 together with the available experimental data and other theoretical values estimated at a high level of theory. The deviations between the experimental enthalpies of formation and those calculated in this work are also illustrated in Figure 1. As can be seen in Table 2 and Figure 1, the difference between the experimental and calculated enthalpies of formation does not exceed 2.5 kJ·mol^{-1} for 12 compounds, namely, **1**, **2**, **7**, **8**, **9**, **11**, **14**, **15**, **20**, **26**, **29**, and **43** (hereinafter, the compound numbers are given according to Table 2), and the experimental $\Delta_fH^\circ_{298}(g)$ values of these furan derivatives are considered as benchmark values. For all of these compounds, with the exception of 2-furanacrylic acid (**20**), the experimental data were obtained from a single study, and therefore, only a comparison with a high-level calculation gives confidence in their accuracy. As for the second experimental value for **20**,[55] it is larger than the calculated one by 43.7 kJ·mol^{-1}, which clearly indicates an error in the experimental data.

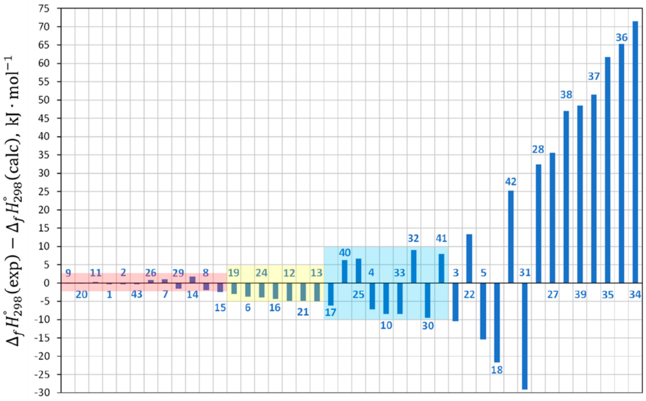

Figure 1. Deviations between the experimental and calculated enthalpies of formation. The blue numbers correspond to the molecule numbering in Table 2. The shaded red, yellow, and blue areas show compounds for which discrepancies between the experimental and calculated values do not exceed 2.5, 5, and 10 kJ, respectively.

The theoretical calculations of the enthalpy of formation were previously performed for almost all of the compounds of this group (Table 2). The value calculated in this study for 2-methylfuran (**2**) is in good agreement with that obtained from CBS-QB3 and CBS-APNO calculations combined with isodesmic reactions,[18] whereas the CCSD(T)-F12b value[16] is noticeably less, although a rather large error (±5 kJ·mol^{-1}) is expected for this value. Values close to the present ones were obtained for **7** and **15** using the atom equivalents approach based on the DLPNO−CCSD(T) method.[17] Good agreement is obtained with the results of G4 calculations[19,20] for **29** and **43** taking into account the calculation errors. The enthalpies of formation obtained for **7**, **8**, **9**, **11**, **14**, and **15** by averaging the results of CBS-QB3, CBS-APNO, and G3 methods[11] are less than those calculated in this study by 4−8 kJ·mol^{-1}, which is most likely due to the inaccuracy of the composite methods used.

Furans with |$\Delta_f H^\circ_{298}$(g, exp) − $\Delta_f H^\circ_{298}$(g, calc)| Values between 2.5 and 5.0 kJ·mol^{-1}. For this group of compounds (**6**, **12**, **13**, **16**, **19**, **21**, and **24**), the discrepancies between the experimental and calculated values are relatively small, and in some cases they can be neglected within the limits of the total error of theory and experiment. Nevertheless, caution should be exercised when using the $\Delta_f H^\circ_{298}$(g, exp) values of these compounds as the references, since they can lead to outliers in the isodesmic reaction calculations.

For example, if furfuryl alcohol (**6**) is used to calculate the enthalpies of formation of furfural (**7**) and 5-hydroxymethylfurfural (**11**) from the following isodesmic reactions:

$$C_5H_4O_2\ \text{(furfural)} + CH_3OCH_3 \rightarrow C_5H_6O_2\ \text{(furfuryl alcohol)} + CH_3C(O)H$$

$$C_6H_6O_3\ \text{(5-hydroxymethylfurfural)} + C_2H_6 \rightarrow C_5H_6O_2\ \text{(furfuryl alcohol)} + CH_3C(O)CH_3$$

the difference between the calculated and experimental $\Delta_f H^\circ_{298}$(g) values of **7** and **11** will be 5.0 and 6.6 kJ·mol^{-1}, respectively, while the use of other furan derivatives gives a good agreement with the experiment for these two molecules (Table S3). The gas-phase enthalpy of formation of **6** used in the above calculations was based on the value of $\Delta_f H^\circ_{298}$(l) determined recently from calorimetric study by Verevkin et al.[12] However, a somewhat larger $\Delta_f H^\circ_{298}$(l) value was obtained in a similar study by Parks et al.[48] (Table 2). Note that the value lying between these two experimental determinations (−277.6 kJ·mol^{-1}) leads to complete agreement between the experimental and calculated gas-phase enthalpies of formation of **6**, and therefore, the value of $\Delta_f H^\circ_{298}$(l) may be further revised. Two other theoretical calculations[17,11] (Table 2) also predict a slightly larger value of the gas-phase enthalpy of formation.

There is a similar situation with 2-furancarboxylic acid (**12**). Of the three published experimental values for $\Delta_f H^\circ_{298}$(cr), two are in good agreement with each other (−498.5 kJ·mol^{-1})[54,48] (Table 2). Similarly, two of the three experimental values of the enthalpy of sublimation (~88 kJ·mol^{-1})[54,56] are in good agreement, while a better agreement between the experimental and calculated gas-phase enthalpies of formation is observed using the seemingly less reliable value of the enthalpy of sublimation (92.8 kJ·mol^{-1}).[55] The experimental values of $\Delta_f H^\circ_{298}$(cr) = −498.5 kJ·mol^{-1} and $\Delta_{sub} H^\circ_{298}$ = 92.8 kJ·mol^{-1} give the value of −405.7 kJ·mol^{-1} for $\Delta_f H^\circ_{298}$(g), which is very close to the calculated $\Delta_f H^\circ_{298}$(g) value of −406.0 kJ·mol^{-1}. This does not exclude the possibility that the experimental data for compound **12** may be revised to some extent. Thus, the experimental $\Delta_f H^\circ_{298}$(g) value of **12**, as well as that of **6**, is considered to be not accurate enough to serve as a benchmark value.

Although the two experimental $\Delta_f H^\circ_{298}$(g) values of 2-furanacrolein (**19**)[58,57] are in fairly good agreement with each other, they are based on conflicting values of $\Delta_f H^\circ_{298}$(cr) and $\Delta_{sub} H^\circ_{298}$. The calculated value, within its uncertainty, is consistent with the experimental data by Ribeiro da Silva et al.[58] The difference of 4−5 kJ·mol^{-1} between the experimental and calculated values for compounds **13**, **16**, **21**, and **24** requires special caution when these compounds are applied as reference species in the thermochemical calculations. The $\Delta_f H^\circ_{298}$(g) values for **12**, **13**, and **16** calculated by averaging the results of the three composite methods[11] are underestimated compared to those obtained in this work and, as noted above, cannot claim high accuracy.

Furans with |$\Delta_f H^\circ_{298}$(g, exp) − $\Delta_f H^\circ_{298}$(g, calc)| Values between 5 and 10 kJ·mol^{-1}. Five of the nine compounds of this group (**30**, **32**, **33**, **40**, and **41**) are the nitro compounds, for which such relatively large errors in the experimental data are often associated with difficulties in handling these energetic materials. Among the remaining four molecules (**4**, **10**, **17**, and **25**), 4,5-dimethylfurfural (**10**) and 2,5-dimethyl-3-acetylfuran (**17**) stand out: the $\Delta_f H^\circ_{298}$(g) values calculated by Simmie et al.[11] agree well with the experimental data compared to the values obtained in this work (Table 2). To support the accuracy of our results, we tried to reproduce the result of Simmie et al.[11] on **10** using CBS-QB3, CBS-APNO, and G3 methods and carried out an additional calculation by the G4 method.[43] All of these calculations were made using, as in ref 11, the isodesmic reaction 4,5-dimethylfurfural + benzene → furfural + 1,3-dimethylbenzene. The average value of CBS-QB3, CBS-APNO, and G3 calculations (−226.4 kJ·mol^{-1}) and the result obtained using the G4 method (−230.7 kJ·mol^{-1}) are in good agreement with the value calculated in this study (−228.6 kJ·mol^{-1}). Thus, the value of −238.3 kJ·mol^{-1} reported in ref 11 is not confirmed by our calculations and most likely contains an error.

Furans with $|\Delta_f H^\circ_{298}(g, exp) - \Delta_f H^\circ_{298}(g, calc)|$ Values Greater than 10 kJ·mol^{-1}. There is definitely an error in the experimental data of compounds belonging to this group (**3**, **5**, **18**, **22**, **27**, **28**, **31**, **34**, **35**, **36**, **37**, **38**, **39**, and **42**; see also the unshaded area in Figure 1). Particular attention should be paid to compounds **20**, **27**, **28**, **31**, and **34**−**39**, for which the discrepancies with calculated values range from 29 to 72 kJ·mol^{-1}. Experimental data of these compounds were obtained in the same research group,[55,60,61,63] and the results may contain the systematic errors. For only one compound, 2-furanacrylic acid (**20**), experimental measurements were also carried out in other work by Ribeiro da Silva and Amaral.[58] As can be seen in Table 2, the $\Delta_f H^\circ_{298}(g)$ value determined in ref 58 agrees well with the value calculated in this work, whereas the experimental value of Sobechko et al.[55] is larger by 43.7 kJ·mol^{-1}. Since the sublimation enthalpies determined in the two studies[55,58] are almost the same, the error can be related to the determination of the combustion energy in ref 55. It should be noted that a sample of **20** was synthesized by the authors, and its composition and purity were not confirmed in any way.

Among the reasons for possible errors in the results[60,61,63] for compounds **27**, **28**, **31**, and **34**−**39**, note that no control for absence of nitrogen oxides (NO and NO_2) was carried out when analyzing the gas combustion products, and therefore, the correction for nitric acid formation was most likely determined inaccurately. In addition, the purity of the substances was not fully confirmed.

Results from Hydrogenation Reactions of Furans. The enthalpy of formation of furan calculated from the hydrogenation reaction (reaction 1 in Table 1) is in good agreement with the experimental value. This isogyric reaction is the most unbalanced among the reactions considered in this work, and therefore, it is interesting to find out whether the hydrogenation reactions with small reference species (H_2, CH_4, C_2H_2, C_2H_4, C_2H_6, H_2O, NH_3, HCN, HNO, HNO_2) work equally well for furan derivatives. Table S3 shows that the difference between the weighted average $\Delta_f H^\circ_{298}(g)$ values and those obtained from hydrogenation reactions does not exceed 2 kJ·mol^{-1} for 38 compounds and that for only five molecules are the discrepancies 2.5−5 kJ·mol^{-1}. This indicates the high accuracy of the method for most of the compounds considered and the possibility of using hydrogenation reactions to reliably predict the enthalpies of formation.

The largest discrepancies are observed for three large molecules (**27**, **28**, and **41**) and two *tert*-butyl derivatives (**4** and **5**). Note that for *tert*-butyl derivatives, large uncertainties were also obtained for the $\Delta_f H^\circ_{298}(g)$ values calculated from isodesmic reactions. Thus, it cannot be ruled out that the DLPNO−CCSD(T) model used in this study is insufficiently accurate for strained *tert*-butyl derivatives. Another note concerns the use of reference species for compounds with nitro groups, for which the best results are achieved when using NH_3 and HNO as the reference rather than HNO_2.

CONCLUSION

High accuracy of the experimental thermochemical data was confirmed for 19 furans (shaded red and yellow areas in Figure 1) using the DLPNO−CCSD(T_1)/CBS method in conjunction with isodesmic-type reactions. For 12 of these compounds, the difference between the calculated and experimental gas-phase enthalpies of formation does not exceed 2.5 kJ·mol^{-1}, and the $\Delta_f H^\circ_{298}(g)$ values of these compounds may serve as benchmark values for use in thermochemical calculations, testing quantum-chemical methods, and modeling and simulation of furan-related combustion applications. Recommended experimental $\Delta_f H^\circ_{298}(g)$ values can be used as a consistent basis to obtain values for other furans of various structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.3c00615.

> Calculated geometries (Table S1), total electronic energies and energy corrections for furans and reference molecules (Table S2), and enthalpies of formation calculated using the DLPNO−CCSD(T_1)/CBS method using different working reactions (Table S3) (PDF)

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Notes

The authors declare no competing financial interest.

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