JOC The Journal of Organic Chemistry
Article
pubs.acs.org/joc

Long Chain Saturated and Unsaturated Carboxylic Acids: Filling a Large Gap of Knowledge in Their Enthalpies of Formation

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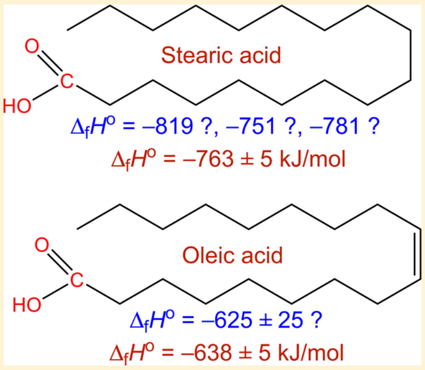
Supporting Information

ABSTRACT: Despite their abundance in nature and their importance in biology, medicine, nutrition, and in industry, gas phase enthalpies of formation of many long chain saturated and unsaturated fatty acids and of dicarboxylic acids are either unavailable or have been estimated with large uncertainties. Available experimental values for stearic acid show a spread of 68 kJ mol^{-1}. This work fills the knowledge gap by obtaining reliable values by quantum theoretical calculations using G4 model chemistry. Compounds with up to 20 carbon atoms are treated. The theoretical results are in excellent agreement with well established experimental values when such values exist, and they provide a large number of previously unavailable values.



INTRODUCTION

Straight chain carboxylic acids are abundant in nature, have both biological and engineering significance, and have found many uses. Long chain saturated and unsaturated acids and their esters play a number of critical biochemical roles in the creation and maintenance of life.[1]

The increasing importance of lipids in the biofuel industry has been noted.[2] There is a wide variety of effects and uses of such molecules. For example, propanoic acid is produced by propionibacteria on human skin and is a cause of acne.[3] It also inhibits the growth of mold and of some bacteria and is used as a preservative (up to 1 w %) in animal feeds.[4] The carboxylic acids have unpleasant odors; caproic acid (hexanoic) is the smell of goats and of ginkgo seeds. However, their esters have pleasant odors and are often used as components of perfumes, cosmetics, and food flavorings because of their fruity odors (propanoate and octanoate esters, ethyl pentanoate, methyl nonanoate). Caprylic acid (octanoic) is an antimicrobial pesticide (weeds, fungi)[5] and the ammonium salt of pelargonic acid (nonanoic) is a herbicide.[6] Undecanoic acid is used as an antifungal agent.[7] Various medicinal compounds are esterified with long chain carboxylic acids to induce lipophilicity, retention in fatty tissue, and slow release as for anabolic steroids (heptanoate of testosterone) and for antipsychotic medications as their decanoates (Bromperidol[8] and Haloperidol[9]). 4-Pentenoic acid can induce Raye's syndrome, a children's decease seriously affecting the brain and liver.[10] Valproic acid (2-*n*-propyl-4-pentenoic), which is used as an anticonvulsive agent, was found to have caused Raye's syndrome in young children with fatal results in at least 80 cases.[11] Aluminum salts of naphthitic acids (containing five- or six-membered rings) and of palmitic acid (hexadecanoic) were the major components of NaPalm used in warfare. Acrylic acid (propenoic) and crotonic acid (*trans*-2-butenoic) and their esters are often used as components of copolymers for various plastics, coatings, hair lacquers and hair-setting lotions,[12] and elastomers. Large amounts of dicarboxylic acids are used in the production of polyesters and nylons. Acids with an even number of carbons are abundant as their triglycerides in fats and oils.

Despite their extensive presence in nature and the many industrial applications of such organic acids, the fundamental physical property of their gas phase enthalpy of formation at 298 K, $\Delta_fH°$, is not known accurately for most of these compounds. For some, reported experimental values have large uncertainties, or have contradictory values. For many, no values exist at all. This is demonstrated for the saturated straight chain carboxylic acids in Table 1, which lists available experimental values from commonly used databases and other sources: the NIST database no. 69,[13] the compilation of Goos et al.,[14] the compilation of Pedley et al.,[15] and that of Verevkin.[16] There are often significant differences, particularly for acids with more than 10 carbons. Notable is the spread of 68 kJ mol^{-1} among the three available values for stearic acid (octadecanoic). As a result the caloric values for dietary triglycerides are unreliable, particularly for the major constituents of acids with 12, 14, 16, and 18 carbon atoms. There are contradictory values of enthalpies of formation available for dicarboxylic acids and very few and contradictory experimental values for unsaturated acids.

Received: November 4, 2016
Published: December 16, 2016

DOI: 10.1021/acs.joc.6b02674
J. Org. Chem. 2017, 82, 673−679

Table 1. Experimental Literature Values of Gas Phase $\Delta_f H°$ in kJ mol^{-1} at 298 K of Saturated Straight Chain Carboxylic Acids and G4 Results[a]

# of C	$\Delta_f H°$[b]	$\Delta_f H°$[c]	$\Delta_f H°$[d]	$\Delta_f H°$[e]	$\Delta_f H°$, G4[f]
2	−433 ± 3	−432.3 ± 0.5	−432.8 ± 1.5	−434.1 ± 0.5	−428.9
3	−455.8 ± 2	−450.9 ± 8	−453.5 ± 0.5	−456.3 ± 0.6	−449.8
4	−475.9 ± 4	−455.83 ± 8	−475.8 ± 4.1	−475.7 ± 1.1	−470.0
5	−491 ± 20	−477.0 ± 8	−491.9 ± 3	−496.4 ± 0.9	−490.9
6	−512 ± 4	−498.2 ± 8	−511.9 ± 3	−514.7 ± 1.8	−511.8
7	−536.5 ± 1.7	−534.3 ± 12.5	−536.2 ± 2.1	−537.3 ± 1.7	−533.7
8	−554.5 ± 1.3	−554.0 ± 12.5	−554.3 ± 1.5	−555.0 ± 1.3	−553.7
9	−575.6 ± 1.0	−573.6 ± 12.5	−577.3 ± 2.1	−577.3 ± 2.1	−574.6
10	−624.5 ± 5.1	−593.7 ± 12.5	−594.9 ± 2.3	−594.9 ± 2.3	−595.5
11		−613.0 ± 12.5	−614.6 ± 1.6		−616.5
12		−633.0 ± 15	−642.0 ± 2		−637.3[g]
13		−660.2 ± 8	−660.2 ± 2.5	−660.2 ± 2.5	−658.2[g]
14		−672.4 ± 15	−693.7 ± 4.1		−679.1[g]
15		−701.2 ± 8	−699.0 ± 4.5	−698.0 ± 4.5	−700.0[g]
16	−730 ± 5.5	−711.7 ± 25	−737.1 ± 4.5		−720.9[g]
17		−731.4 ± 8			−741.8[g]
18	−819.1 ± 5.5	−751.0 ± 31	−781.2 ± 4.7		−762.7[g]
19			−785.3 ± 5.6	−785.4 ± 5.6	−783.6[g]
20	−812.6 ± 7.5	−790.4 ± 22.6	−812.4 ± 7.7		−804.5[g]

[a] Acetic acid to eicosanoic acid, $C_2H_4O_2$ to $C_{20}H_{40}O_2$. [b] Ref 13. [c] Ref 14. [d] Ref 15. [e] Ref 16. [f] Results of the G4 calculation by the atomization method. [g] Extrapolated by eq 2.

RESULTS AND DISCUSSION

Recourse to quantum theoretical calculations is useful when available experimental data are in conflict or when experiment is too difficult to perform accurately, as is often the case with long chain carboxylic acids. The performances of various composite theoretical methods, CBS-QB3, CBS-APNO, G3, and G4 have been evaluated and the best method was found to be G4,[17] which is also the most computationally demanding among them, particularly for the large molecules treated in this work.

To establish more reliable values of gas phase enthalpies of formation at 298 K and 1 bar pressure, $\Delta_f H°$, of these important compounds, we performed quantum theoretical calculations using the model chemistry of the composite G4 method,[18] by the application of Gaussian-09,[19] the zero point corrected electronic energy at 0 K and the enthalpy at 298 K for each molecule. The theoretical method calculates enthalpies of formation from a standard state of the constituent nucleons and electrons. The G4 values for such enthalpies of formation of C, H, and O are −37.831808, −0.499060, and −75.043141, respectively, in units of hartrees, E_h. Conventionally, enthalpies of formation are calculated in terms of the constituent elements in the standard state. The G4 values in E_h are converted to kJ mol^{-1} by the atomization method using the experimental $\Delta_f H°$ of the atoms in their ground states at 298 K and 1 bar pressure:[13] $\Delta_f H°[C]$ = 716.68 kJ mol^{-1}, $\Delta_f H°[H]$ = 217.998, and $\Delta_f H°[O]$ = 249.18. Details of the conversion procedure are given in the Supporting Information section.

We report here results for saturated straight chain carboxylic and dicarboxylic acids, and straight chain monounsaturated acids both for the trans and cis configurations. The theoretical values are compared to existing experimental ones when the latter are available.

Method. The molecules were constructed using the software PCMODEL.[20] The resulting structure was geometry-optimized using Allinger's MM3.[21] The result was transferred to the Comet computer at the San Diego Supercomputing Center[22] and used as an input file to the Gaussian G4 program.[18,19] After a successful run, the output file was searched for imaginary roots, which were rare and were easily eliminated by modifying the input file and repeating the run. Starting with the structure of the simplest member of a series, more complex members were constructed by building on the previous member. More details are available in the Supporting Information section.

Saturated Carboxylic Acids. Benchmarking by comparison with experimental values is important for validating the theoretical results and establishing their level of accuracy. For the saturated straight chain carboxylic acids acetic through undecanoic, the G4 values in E_h are given in the Supporting Information. For butanoic acid through undecanoic, the G4 values in hartees are described analytically by eq 1, where $H°$ is the enthalpy of formation in E_h at 298 K and n is the number of carbon atoms.

$$H° = -150.423320 - 39.276917 \times n \qquad (1)$$

Deviations of the values of eq 1 from the G4 values are less than 0.000051 E_h (0.13 kJ mol^{-1}). The G4 values in E_h were converted to kJ mol^{-1} and are given in Table 1, along with experimental values from four commonly used data sources. For acetic acid (ethanoic) through capric acid (decanoic) experimental values are available from all four sources, but they are not always in agreement. The results we obtain via the G4 calculation are in good agreement with most of the available experimental values for this group of acids. The largest acid for which we were able to allocate computer resources for G4 calculations is undecanoic and the calculated value of −616.4 kJ mol^{-1} is in agreement with the two available experimental values of −613 ± 13 and −614.6 ± 1.6. The data of Table 1 from acetic to undecanoic acid are shown in Figure 1 to illustrate the type of agreement with experiment and the scatter of some of the available experimental values.

For acids with more than 13 "heavy" atoms, accurate calculations (G4 or W1BD) become computationally expensive

DOI: 10.1021/acs.joc.6b02674
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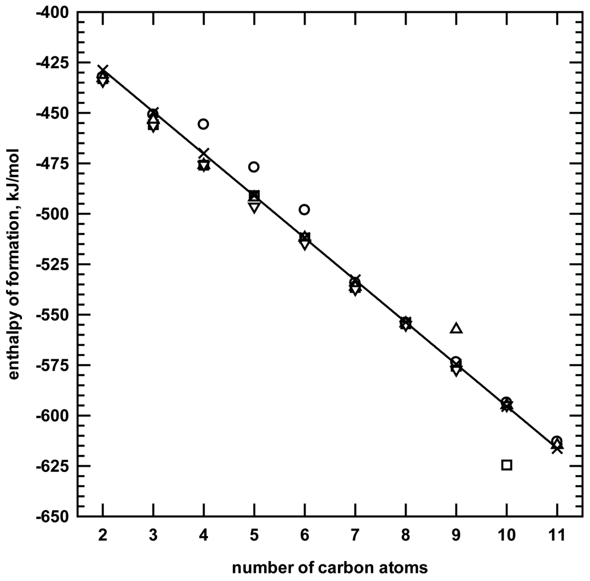

Figure 1. Gas phase $\Delta_f H°$ of straight chain carboxylic acids (C_2 to C_{11}) plotted against the number of carbon atoms. Square symbols, ref 13; circles, ref 14; up-pointing triangles, ref 15; down-pointing triangles, ref 16; and ×, this work G4 results. The line is defined by the G4-derived results for butanoic acid through undecanoic.

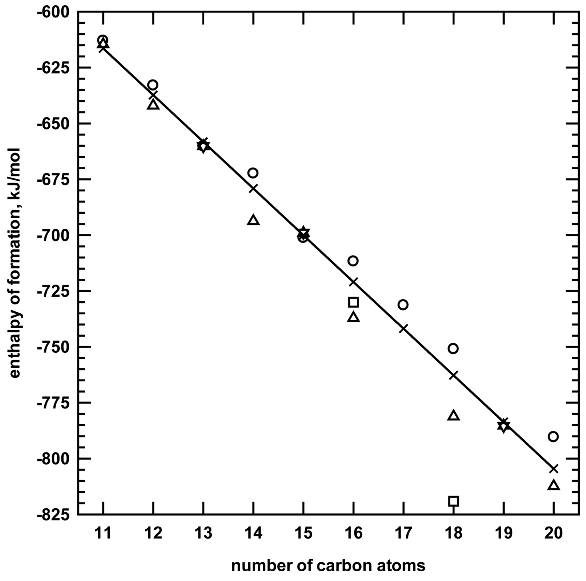

Figure 2. Gas phase $\Delta_f H°$ of straight chain carboxylic acids (C_{11} to C_{20}) plotted against the number of carbon atoms. Square symbols, ref 13; circles, ref 14; up-pointing triangles, ref 15; down-pointing triangles, ref 16; and ×, this work G4 extrapolated results. The line is defined by the G4 results.

and this limits the size of the molecules that can be modeled accurately with existing resources. For saturated acids with more than 11 carbons, we took advantage of the expected regularity with which enthalpies of formation change as a function of the number of carbon atoms. The G4 enthalpy of formation changes by a constant −39.276917 ± 0.000012 E_h, equivalent to −20.90 ± 0.001 kJ mol^{-1}, for each additional CH_2 group for the saturated straight chain acids from butanoic through undecanoic. This regularity is expected from the well-known success of group additivity approaches.[23,24] However, to establish an accurate experimentally based group additivity approach for extrapolations one needs to have a series of reliable experimental values for the lower members of a series. This is not the case for available experimental values of the compounds of this work. Even with the saturated carboxylic acids for which many experimental values are available, there is considerable scatter as seen in Table 1 and in Figures 1 and 2. Treated by the atomization method, the G4 values converted to kJ mol^{-1} are described analytically by eq 2, where $\Delta_f H°$ is the gas phase value at 298 K and n is the number of carbon atoms of saturated straight chain carboxylic acids. The values obtained via eq 2 differ by not more than 0.1 kJ mol^{-1} from all those listed in Table 1 by the G4 atomization procedure. In effect, eq 2 is a recasting of eq 1 in the more familiar units of kJ mol^{-1}. Were $\Delta_f H°$ for acetic and propanoic acids to be obtained by eq 2, the value so obtained would underestimate their G4 stability by only 0.45 kJ mol^{-1} and 0.64, respectively.

$$\Delta_f H° = -386.50 - 20.900 \times n \tag{2}$$

We used eq 2 to obtain extrapolated gas phase $\Delta_f H°$ values at 298 K from dodecanoic acid up to arachidic acid (eicosanoic) in kJ mol^{-1} as shown in Table 1. Such long extrapolations may compound small errors or uncertainties in the atomization procedure and yield unreliable results. The accuracy of the extrapolations can be judged by comparison with the most recent set of experimental values reported for carboxylic acids,[16] which include three acids in the region of our extrapolation. The value reported for tridecanoic acid is −660.2 ± 2.5 kJ mol^{-1} experimentally and −658.2 by our extrapolation; reported for pentadecanoic acid is −698.0 ± 4.5 experimentally and −700.0 by extrapolation; and reported for nonadecanoic acid is −785.4 ± 5.6 experimentally and −783.6 by extrapolation. For molecules of this size, the agreement of the extrapolated theoretical values is remarkable. The available experimental values and our results for undecanoic through eicosanoic acid are shown in Figure 2. The large scatter of experimental values is evident and the scatter of the three available values for stearic acid (octadecanoic) is surprisingly large for such an essential part of dietary fats and oils. Beyond eicosanoic acid experimental values with large uncertainties exist for two acids.[14] For behenic acid (docosanoic, $C_{22}H_{44}O_2$): $\Delta_f H°$ = −845.3 ± 35 kJ mol^{-1}; eq 2 yields −846.3. For lignoceric acid (tetracosanoic, $C_{24}H_{48}O_2$): $\Delta_f H°$ = −886.6 ± 40 kJ mol^{-1}; eq 2 yields −888.1.

Dicarboxylic Acids. In addition to eq 2, an accurate description of the $\Delta_f H°$ of saturated straight chain carboxylic acids is also given by eq 3, where $\Delta_f H°[RCH_3]$ is the enthalpy of formation obtained via G4 for the straight chain alkane with the same number of carbons as the carboxylic acid.

$$\Delta_f H°[RCO_2H] = \Delta_f H°[RCH_3] - 346.74 \text{ kJ mol}^{-1} \tag{3}$$

We have reported G4 values at 289 K for the straight chain alkanes ethane through dodecane.[25] The G4 results in E_h are described analytically by $H° = -1.179366 - 39.276917 \times n$, where n is the number of carbon atoms. Converted to kJ mol^{-1} the results are described by eq 4. The values obtained for alkanes generally agree with experimental values to within the usual limits of uncertainty in the experimental values up to eicosane, n-$C_{20}H_{42}$, for which the extrapolated G4-derived value is −457.92 kJ mol^{-1} compared to the experimental value of −455.8 ± 3.[13,14]

$$\Delta_f H°[\text{alkane}] = -42.175 - 20.900 \times n \tag{4}$$

Table 2. Experimental Literature Values of Gas Phase $\Delta_fH°$ in kJ mol^{-1} at 298 K of Saturated Straight Chain Dicarboxylic Acids and G4 Results[a]

# of C	$\Delta_fH°$[b]	$\Delta_fH°$[c]	$\Delta_fH°$[d]	$\Delta_fH°$[e]	$\Delta_fH°$, G4[f]
4	−816.8 ± 3	−817.7 ± 0.6		−818.2 ± 3.3	−819.2
5		−837.0 ± 8		−840.2 ± 1.7	−840.2
6			−865.0 ± 2.6	−860.1 ± 1.5	−861.1
7				−869.5 ± 1.6	−882.0
8			−894.9 ± 4.0	−890.2 ± 4.1	−902.9
9				−894.4 ± 2.6	−923.8
10	−921.6 ± 3		−921.9 ± 3.6	−917.3 ± 3.6	−944.7
11				−936.9 ± 3.2	−965.6
12	−977.0 ± 4.2		−976.9 ± 4.1	−972.4 ± 4.4	−986.5

[a] Butanedioic acid to dodecanedioic, $C_4H_6O_4$ to $C_{12}H_{22}O_4$. [b] Ref 13. [c] Ref 14. [d] Ref 15. [e] Ref 28. [f] G4 results by eq 4 and 5.

Eq 3 demonstrates that conversion of a CH_3 group of a straight chain alkane to a CO_2H group causes a decrease of 346.74 kJ mol^{-1} in the $\Delta_fH°$ of the parent alkane. When the two CH_3 groups of a straight chain alkane are converted to carboxylic acids, eq 5 yields the gas phase enthalpy of formation of the dicarboxylic acid in kJ mol^{-1}.

$$\Delta_fH°[HO_2C(CH_2)_nCO_2H] = \Delta_fH°[CH_3(CH_2)_nCH_3] + (-346.74 \times 2) \qquad (5)$$

Eq 5 is used to calculate the gas phase $\Delta_fH°$ of straight chain dicarboxylic acids from succinic acid (butanedioic) up to sebasic acid (dodecanedioic). The relationship of eq 5 is valid only when the two carboxyl groups are separated by at least two CH_2 groups. It is not valid for oxalic acid (ethanedioic) and for malonic acid (propanedioic) where the two carboxy groups are in close proximity. It has been reported that α -dicarbonyls are "destabilized" because of repulsion between two adjacent carbonyl carbons bearing substantial positive charge, despite the presence of formal conjugation in the O═C−C═O moiety. 2,3-Butanedione is destabilized[26] by 24.7 kJ mol^{-1} and oxalic acid[27] by a remarkable 59 kJ mol^{-1} relative to "normal" behavior of isolated functional groups assumed by group additivity approaches. Using eqs 4 and 5 for oxalic acid leads to $\Delta_fH° = -777.5$ kJ mol^{-1} compared to the experimental value of -721.4 ± 2.1,[14] for an apparent destabilizing repulsion of 56 kJ mol^{-1}. An experimental value of $\Delta_fH° = -779.7 \pm 0.8$ kJ mol^{-1} has been reported[28] for malonic acid, while eqs 4 and 5 yield −798.3 for a substantially decreased repulsion destabilization of 18.5 kJ mol^{-1}. The results for the saturated dicarboxylic acids from succinic (butanedioic) to dodecanedioic are listed in Table 2 and shown graphically in Figure 3. There is excellent agreement with available experimental values for succinic, valeric (pentanoic), and adipic (hexanedioic) acids, but deviations appear beyond six carbons.

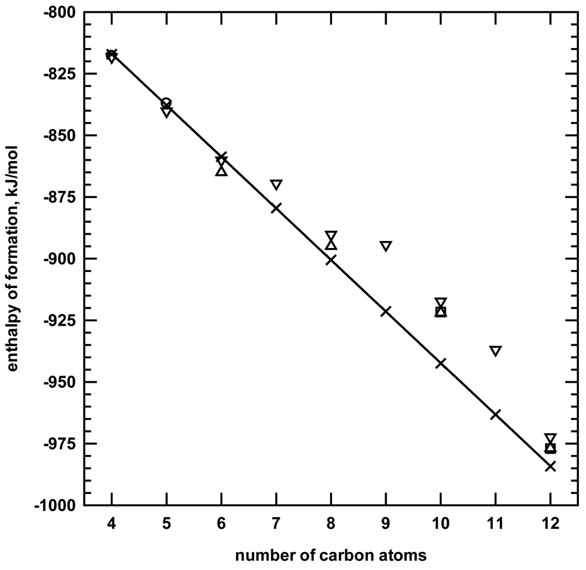

Figure 3. Gas phase $\Delta_fH°$ at 298 K of saturated straight chain dicarboxylic acids (C_4 to C_{12}) plotted against the number of carbon atoms. Square symbols, ref 13; circles, ref 14; up-pointing triangles, ref 15; down-pointing triangles, ref 28; and × , this work G4 results. The line is defined by the G4 results.

Figure 3 shows deviations from a regular monotonic decrease in $\Delta_fH°$ beyond adipic acid. These deviations have been noted previously and rationalized in terms of possible internal hydrogen bonding for dicarboxylic acids of more than 6 carbons.[28] Hydrogen bonding is unlikely in the gas phase and heptanedioic acid would form a 10-membered ring. If such hydrogen bonding were occurring, additional stability would be gained and $\Delta_fH°$ would be more negative than otherwise expected. The fact, evident in Figure 3, is that the reported experimental points beyond adipic acid lie above the theoretical G4 line that does not include internal hydrogen bonding and that fits the first three members of the series. The reported experimental values indicate lesser, not greater, stability than would be normally expected. Roux at al. have found that solid−solid phase transitions in heptanedioic and nonanedioic acids occur and have an influence on the enthalpies of sublimation when these are measured directly.[29] If contaminated enthalpies of sublimation are used to convert solid phase enthalpies of formation to gas phase values, these values will be compromised. It was also concluded that evidence for cyclic forms appears only beyond undecanedioic acid.[28] Such complications may be related to the deviations that exist between the G4-derived values and previously reported gas phase data. The deviations between previously reported experimental values and the G4-derived value are smallest for dodecanedioic acid, the last member of the series studied.

Unsaturated Carboxylic Acids. These are quite common in nature and there are few reliable experimental values available of their gas phase enthalpies of formation. Some such acids are described as "essential" because they must be taken in the diet and are needed for human growth and development. We have obtained G4-derived gas phase enthalpies of formation at 298 K for all trans monounsaturated straight chain acids up to 10 carbons with the double bond located at all possible positions. The G4 results, converted by the atomization method to kJ mol^{-1}, are given in Table 3, where the position

Table 3. G4 Calculated Gas Phase $\Delta_f H°$ in kJ mol^{-1}at 298 K of All trans Monounsaturated Straight Chain Acids from Propenoic to All of the *trans*-9-Decenoic Acids[a]

# of C	posit. 2	posit. 3	posit. 4	posit. 5	posit. 6	posit. 7	posit. 8	posit. 9
3	−319.5							
4	−356.1	−339.4						
5	−375.6	−370.6	−360.7					
6	−397.1	−390.3	−392.4	−382.6				
7	−418.2	−411.7	−412.2	−414.2	−404.2			
8	−439.2	−432.7	−432.7	−434.0	−435.4	−425.4		
9	−460.1	−453.8	−454.7	−455.1	−455.3	−456.5	−446.7	
10	−480.9	−474.7	−475.6	−475.9	−476.6	−476.3	−477.4	−467.6

[a] The column headings indicate the number of carbons atoms and the position of the double bond.

indicates IUPAC numbering: position 1 is the carboxylic carbon. For example, *trans*-7-decenoic acid is located at the intersection of column "posit. 7" and row "10", $\Delta_f H° = -476.3$ kJ mol^{-1}. The G4 results in E_h are given in the Supporting Information

Experimental $\Delta_f H°$ values were located for only two of the compounds of Table 3. For acrylic acid, ref 4 lists three values −330.7 ± 4.2, − 324.7, − 336.9 ± 2.3 and ref 13 lists −326.1 ± 8 kJ mol^{-1}; the last value, within its stated uncertainty, is consistent with the G4 value of −319.5 in Table 3. For crotonic acid (*trans*-2-butenoic), an experimental $\Delta_f H° = -363.1 \pm 8$ kJ mol^{-1} is available[14] and is barely within the limit of its uncertainty with the G4 value of −356.2 in Table 3. No experimental values were located for all other entries of Table 3.

For all straight chain *trans*-2-alkenoic acids from 4 to 10 carbons, $\Delta_f H°$ values in kJ mol^{-1} are given analytically by eq 6, where n is the number of carbon atoms. The equation matches the corresponding G4-derived values of Table 3 with an average deviation of 0.33 kJ mol^{-1} and a maximum deviation of 0.66.

$$\Delta_f H° = -271.76 - 20.900 \times n \tag{6}$$

For all straight chain alkenoic acids from 4 to 10 carbons with the double bonds at the ω position (terminal), $\Delta_f H°$ values in kJ mol^{-1} are given analytically by eq 7, where n is the number of carbon atoms. The equation matches the corresponding G4-derived values of Table 3 with an average deviation of 0.84 kJ mol^{-1} and a maximum deviation of 1.88.

$$\Delta_f H° = -257.79 - 20.900 \times n \tag{7}$$

For all other straight chain trans alkenoic acids, $\Delta_f H°$ in kJ mol^{-1} is given analytically by eq 8, where n is the number of carbon atoms. The equation matches the corresponding G4-derived values of Table 3 with an average deviation of 0.90 kJ mol^{-1} and a maximum deviation of 1.99.

$$\Delta_f H° = -266.78 - 20.900 \times n \tag{8}$$

Acrylic acid does not fit into any of the above three categories because it is unique in being both a 2-alkenoic acid and one with a terminal double bond. Enthalpies of hydrogenation, ΔH_{hyd}, are given by the difference of the G4 values of $\Delta_f H°$ between the saturated and the corresponding alkenoic acids from Tables 1 and 3. On doing so, we find that ΔH_{hyd}[acrylic acid] = $\Delta_f H°$[propanoic acid] − $\Delta_f H°$[acrylic acid] = −449.8 − (−319.5) = −130.3 kJ mol^{-1} is not significantly different from ΔH_{hyd} of the terminal double bonds of 3-butenoic acid or of 4-pentenoic acid −130.6 and −130.2, respectively. The formal conjugation of the C═C−C═O moiety does not seem to impart any stabilization to acrylic acid. However, the double bond at the 2 position of all other alkenoic acids is more stable than other internal trans double bonds by an average of 5 kJ mol^{-1}, as seen from the difference of the intercepts of eq 6 and eq 8. As expected, terminal double bonds are the least stable type being more unstable than trans double bonds by 9 kJ mol^{-1} as seen by comparing the intercepts of eqs 7 and 8, as has been known from many experimental enthalpies of hydrogenation of such alkenes.[30]

The relation of eq 8 was used to extrapolate to longer monounsaturated carboxylic acids, many of which are of biological interest and for which the few available values often have very large stated uncertainties. While eq 8 is based only on trans unsaturated acids, the values obtained can be converted to the corresponding cis configuration. The G4 results of all monounsaturated straight chain cis and trans alkenes up to $C_{12}H_{24}$ define a greater stability for the trans isomer by 5.0 ± 0.4 kJ mol^{-1}.[25] By adding 5.0 ± 0.4 kJ mol^{-1} to the intercept of eq 8 for the *trans*-alkenes one obtains the values of the corresponding cis isomers by eq 9.

$$\Delta_f H° = -261.78 - 20.900 \times n \tag{9}$$

Experimental measurements are available for some straight chain cis and trans fatty acids with more than 10 carbons. Our results for these cases are compared to experiment below.

Extrapolating eq 8 to elaidic acid (*trans*-9-octadecenoic) yields $\Delta_f H° = -642.98$ kJ mol^{-1}, but no experimental gas phase value was found for this acid. However, the enthalpy of hydrogenation of elaidic acid has been measured[31] as $\Delta H_{hyd} = -120.2 \pm 2$ kJ mol^{-1}. Therefore, $\Delta_f H°$[elaidic acid] = $\Delta_f H°$[octadecanoic acid] − ΔH_{hyd}[elaideic acid]. With the G4 value of octadecanoic acid from Table 1 and the experimental ΔH_{hyd}, we obtain − 762.7 − (−120.2 ± 2) = −642.5 ± 2 kJ mol^{-1}, consistent with the value obtained by using only extrapolated theoretical values.

$\Delta_f H°$ for oleic acid (*cis*-9-octadecenoic) is obtained by eq 9, which yields $\Delta_f H°$[oleic acid] = −637.98 ± 0.4 kJ mol^{-1}. The enthalpy of hydrogenation of oleic acid has been measured[31] as $\Delta H_{hyd} = -124.4 \pm 1.2$ kJ mol^{-1}. With the G4 value of octadecanoic acid from Table 1 and the experimental ΔH_{hyd}, we obtain $\Delta_f H° = -762.7 - (-124.4 \pm 1.2) = -638.3 \pm 1.2$ kJ mol^{-1}. Again, the values obtained by using only extrapolated theoretical values or by including experimental values of ΔH_{hyd} are consistent. The above examples should lend confidence in the procedures followed in this work. There is an experimental value[14] of $\Delta_f H°$[oleic acid] = −624.7 ± 25 kJ mol^{-1}, which, within its stated large uncertainty, is in agreement with the G4-derived value.

Palmitoleic acid (*cis*-9-hexadecenoic) is also of interest for being a major component of fats and oils. By eq 9,

DOI: 10.1021/acs.joc.6b02674
J. Org. Chem. 2017, 82, 673−679

$\Delta_f H°$[palmitoleic acid] = −596.18 kJ mol^{-1}. The enthalpy of hydrogenation of palmitoleic acid has been measured[31] as ΔH_{hyd} = −125.1 ± 1.0 kJ mol^{-1}. With the G4 value of hexadecanoic acid from Table 1 and the experimental ΔH_{hyd}, we obtain − 720.9 − (−125.1 ± 1.0) = −595.8 ± 1.0 kJ mol^{-1}. Again, the values obtained by using only extrapolated theoretical values or by including experimental values of ΔH_{hyd} are consistent. There is an experimental value of $\Delta_f H°$[palmitoleic acid] = −585.3 ± 25,[14] which, within its stated large uncertainty, is in agreement with the G4 value.

An experimental value of $\Delta_f H°$ = −605.4 ± 25 kJ mol^{-1} is available[14] for margaroleic acid (*cis*-9-heptadecenoic). By eq 9, we obtain the more reliable value of $\Delta_f H°$[margaroleic acid] = −617.1.

Similar extrapolations by eq 6, 7, 8, or 9 will provide reliable values for all other monounsaturated acids for which experimental values are not available. The above comparisons with existing reliable experimental values of saturated and of dicarboxylic acids leads us to estimate that calculated so values will be accurate to well within about ±6 kJ mol^{-1} for monounsaturated acids at least up to 20 carbon atoms. For example, using eq 9 for myristoleic acid (*cis*-9-tetradecenoic) yields $\Delta_f H°$ = −554.4 kJ mol^{-1}. No experimental value is available for this acid, which is relatively rare in nature and has been reported to have activity against a type of human prostate cancer cells.[32]

■ CONCLUSION

Values of gas phase enthalpies of formation at 298 K have been obtained by G4-derived calculations for all saturated and monounsaturated straight chain cis and trans carboxylic acids of up to 20 carbon atoms and for dicarboxylic acids up to 12 carbons. For many members of this class of important compounds the values provided in this work are the only ones extant. In cases where well established experimental values exist, they support the reliability of the results we report.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02674.

> Details of the methods used to obtain the G4 results, of their conversion from units of hatrees to kJ mol^{-1}, and G4 values in hartrees as obtained for carboxylic acids and for *trans*-alkenoic acids (PDF)

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are happy to acknowledge support by a grant of computer time by the National Science Foundation. The calculations were performed through the courtesy of XSEDE.org.[33] We thank the University of Washington for technical support and the Whiteley Foundation for a fellowship during which some of this work was carried out.

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