Enthalpies of Formation, Bond Dissociation Energies, and Molecular Structures of the *n*-Aldehydes (Acetaldehyde, Propanal, Butanal, Pentanal, Hexanal, and Heptanal) and Their Radicals

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Aldehydes are important intermediates and products in a variety of combustion and gas-phase oxidation processes, such as in low-temperature combustion, in the atmosphere, and in interstellar media. Despite their importance, the enthalpies of formation and bond dissociation energies (BDEs) for the aldehydes are not accurately known. We have determined enthalpies of formation for acetaldehyde, propanal, and butanal from thermodynamic cycles, using experimentally measured reaction and formation enthalpies. All enthalpy values used for reference molecules and reactions were first verified to be accurate to within around 1 kcal mol^{-1} using high-level ab initio calculations. Enthalpies of formation were found to be −39.72 ± 0.16 kcal mol^{-1} for acetaldehyde, −45.18 ± 1.1 kcal mol^{-1} for propanal, and −49.27 ± 0.16 kcal mol^{-1} for butanal. Enthalpies of formation for these three aldehydes, as well as for pentanal, hexanal, and heptanal, were calculated using the G3, G3B3, and CBS-APNO theoretical methods, in conjunction with bond-isodesmic work reactions. On the basis of the results of our thermodynamic cycles, theoretical calculations using isodesmic work reactions, and existing experimental measurements, we suggest that the best available formation enthalpies for the aldehydes acetaldehyde, propanal, butanal, pentanal, hexanal, and heptanal are −39.72, −45.18, −50.0, −54.61, −59.37, and −64.2 kcal mol^{-1}, respectively. Our calculations also identify that the literature enthalpy of formation of crotonaldehyde is in error by as much as 1 kcal mol^{-1}, and we suggest a value of −25.1 kcal mol^{-1}, which we calculate using isodesmic work reactions. Bond energies for each of the bonds in the aldehydes up to pentanal were calculated at the CBS-APNO level. Analysis of the BDEs reveals the $R-CH_2CH=O$ bond to be the weakest bond in all aldehydes larger than acetaldehyde, due to formation of the resonantly stabilized vinoxy radical (vinyloxy radical/formyl methyl radical). It is proposed that the vinoxy radical as well as the more commonly considered formyl and acetyl radicals are important products of aldehyde combustion and oxidation, and the reaction pathways of the vinoxy, formyl, and acetyl radicals are discussed. Group additivity values for the carbon−oxygen−hydrogen groups common to the aldehydes are also determined. Internal rotor profiles and electrostatic potential surfaces are used to study the dipole induced dipole−dipole interaction in the synperiplanar conformation of propanal. It is proposed that the loss of this dipole−dipole interaction in $RC^{\bullet}HCH_2CH=O$ radicals causes a ca. 1−2 kcal mol^{-1} decrease in the aldehyde C−H and C−C bond energies corresponding to $RC^{\bullet}HCH_2CH=O$ radical formation.

Introduction

Aldehydes are a major class of organic compounds which commonly occur as key reactants, intermediates, and products in a diverse range of gas- and liquid-phase reaction systems. Aldehydes will also be primary intermediates in the oxidation of alcohol biofuels, as the carbon bonded to the OH group has a weakly bound hydrogen atom that will undergo abstraction via radicals to form a hydroxy methyl radical. This hydroxy radical will undergo unimolecular elimination to the aldehyde + H with a low barrier. The radicals formed from aldehydes, such as the formyl, acetyl, and vinoxy radicals, are also known to be common reaction intermediates. Aldehydes are especially important during the low-temperature stages of combustion,[1] and have been proposed as fuels for cool flame combustion processes.[2] The tautomerization of vinyl alcohols (enols), which have recently been identified as important combustion intermediates,[3] leads to aldehyde formation with a relatively low barrier to reaction.[4] Aldehydes formed during combustion contribute to atmospheric pollution and are involved in tropospheric oxidation reactions.[5] A variety of ketones and aldehydes have also been detected in interstellar media,[6] where they are thought to react on grain surfaces to provide complex organic molecules. Accurate knowledge of the formation enthalpies, enthalpy increments with increased carbons, and bond energies of the aldehydes is of value in understanding, and developing kinetic models for, a variety of organic synthesis, combustion, and atmospheric oxidation processes.

There is disagreement in the reported experimental gas-phase enthalpies of formation for acetaldehyde, propanal, and butanal, where differences span a range of at least 1 kcal mol^{-1}. In addition, bond dissociation energies (BDEs) for many of the bonds in these aldehydes are unknown. To our knowledge, the enthalpies of formation of pentanal, hexanal, and heptanal have only been measured once, at −54.61 ± 0.41,[7] −59.37 ± 0.38,[8] and −63.1 kcal mol^{-1},[9] respectively. The enthalpy of formation

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TABLE 1. Reactions Involving Acetaldehyde, Propanal, and Butanal and Their Experimental $\Delta_{rxn}H°_{298}$ (kcal mol^{-1}) Values

	reaction	$\Delta_{rxn}H°_{298}$	ref
	Acetaldehyde		
A1	$CH_3CH{=}O + H_2 \rightleftharpoons CH_3CH_2OH$	−16.51 ± 0.1	9
	Propanal		
P1	$CH_3CH_2CH{=}O + H_2 \rightleftharpoons CH_3CH_2CH_2OH$	−15.72 ± 0.16	14
P2	$CH_3CH_2CH{=}O \rightleftharpoons$ *cyclo*-$CH(CH_3)OCH_2$	23.6	23
	Butanal		
B1	$CH_3CH_2CH_2CH{=}O \rightleftharpoons CH_3CH{=}CHCH{=}O + H_2$	24.91 ± 0.1	24
B2	$CH_3CH_2CH_2CH{=}O + H_2 \rightleftharpoons CH_3CH_2CH_2CH_2OH$	−16.85 ± 0.3	14
B3	$CH_3CH_2CH_2CH{=}O + 2CH_3OH \rightleftharpoons CH_3CH_2CH_2CH(OCH_3)_2 + H_2O$	−14.1 ± 0.3	25

of acetaldehyde has been measured as −40.80 ± 0.35 kcal mol^{-1} by Wiberg et al.[10] The thermochemical reference text of Pedley et al.[7] recommends an enthalpy of −39.70 ± 0.12 kcal mol^{-1}. da Silva et al.[11] suggested that this later value was correct, as it provided an accurate enthalpy for formaldehyde from an isodesmic reaction scheme. Recently, Carstenson et al.[12] have calculated the formation enthalpy of acetaldehyde to be −40.76 kcal mol^{-1} from CBS-QB3 calculations. The enthalpy of formation of propanal has also been measured several times, with little agreement between the reported values. The earliest measurement appears to be that of Tjebbes,[13] who found it to be −45.9 kcal mol^{-1}. Subsequently, this value was determined as −45.55 ± 0.21 kcal mol^{-1} by Buckley and Cox,[14] and −44.46 ± 0.36 kcal mol^{-1} by Connett (at 473−524 K).[15] More recently, Wiberg et al.[10] have found the enthalpy of propanal to be −45.09 ± 0.18 kcal mol^{-1}. The enthalpy of formation of butanal has been determined as −48.85 ± 0.34 by Buckley and Cox[14] and −50.61 ± 0.22 kcal mol^{-1} by Wiberg et al.[10] We feel that the values and differences between consecutive members in the series of normal aldehydes can be improved and trends in bond energy evaluated.

Recently, we were able to determine an accurate enthalpy of formation for formaldehyde through a series of thermodynamic cycles utilizing experimental reaction and formation enthalpies from the literature, and computational chemistry.[11] Computationally, enthalpies of formation were determined using both atomization and isodesmic work reactions, and the use of isodesmic reactions was found to provide the most accurate results, due to the cancellation of some systematic computational errors. The use of isodesmic reactions in conjunction with high-level theoretical methods has been used extensively to compute accurate thermochemical properties.[11,16,17] In this study, the enthalpies of acetaldehyde, propanal, butanal, pentanal, and hexanal are evaluated from both existing thermochemical data and from ab initio calculations utilizing isodesmic work reactions. BDEs for all bonds in formaldehyde, acetaldehyde, propanal, butanal, and pentanal are also calculated using the highly accurate ab initio CBS-APNO method. It is hoped that our results will provide precise thermochemical information for constructing combustion and oxidation models, while also giving insight into the gas-phase reaction mechanisms of this important class of compounds.

Computational Methods

The computational methods G3,[18] G3B3,[19] and CBS-APNO[20] (where computationally feasible) were used to study enthalpies of formation. The G3 method involves an initial geometry optimization and frequency calculation at the HF/6-31G(d) level, to provide zero-point energy and thermochemical corrections. An MP2/6-31G(d) geometry optimization is then performed, and this geometry is used for a QCISD/6-31G(d) energy calculation correcting for the level of theory, followed by an MP4-level basis set correction. The G3B3 method is similar to the G3 method, but the HF and MP2 calculation steps are replaced with a B3LYP/6-31G(d) optimization and frequency calculation. The CBS-APNO method performs an initial geometry optimization and frequency calculation at the HF/6-311G(d,p) level, followed by a higher-level QCISD/6-311G(d,p) geometry optimization. A single point energy calculation is then performed at the QCISD/ 6-311++G(2df,p) level, followed by extrapolation to the complete basis set limit. Due to the large computational requirements of the QCISD/6-311++G(2df,p) energy calculation in the CBS-APNO method, this method was not applicable to the largest molecules used in this study. Optimized geometries of the aldehydes at the HF/6-31G(d), MP2/6-31G(d), B3LYP/6-31G(d), HF/6-311G(d,p), and QCISD/6-311G(d,p) levels are included in the Supporting Information. Corrections to molecular energies due to hindered internal rotations were calculated using the formalism of Ayala and Schlegel[21] (energy corrections are listed in the Supporting Information). All calculations were performed using the Gaussian 03 suite of programs.[22] Energies from the computational chemistry calculations are reported in the Supporting Information.

TABLE 2. Comparison between Computational and Experimental Reaction Enthalpies and Average Absolute Error[a]

	exptl	CBS-APNO	G3	G3B3	error
A1	−16.51	−16.5	−15.9	−15.8	0.4
P1	−15.72	−16.0	−15.4	−15.4	0.1
P2	23.6	22.1	22.4	22.4	1.3
B1	24.91	25.6	24.7	24.5	0.0
B2	−16.85	−16.1	−15.5	−15.4	1.2
B3	−14.1	na	−15.7	−15.5	1.5

[a] All values in kcal mol^{-1}.

Results and Discussion

Experimental Enthalpies of Formation. The enthalpy of formation of a molecule can be obtained from the enthalpy of a reaction involving that molecule and the enthalpies of formation for all other species in the reaction. Such a thermodynamic cycle can provide very accurate enthalpies of formation, as experimentally measured enthalpies can have uncertainties of 0.1 kcal mol^{-1} or lower. However, the uncertainties quoted for experimental enthalpies are often incorrect, as it is not uncommon to find two enthalpy values for a molecule which differ by more than the sum of their quoted errors. Therefore, in this study we will first evaluate the accuracy of these experimental enthalpy values using computational techniques, which are capable of calculating enthalpies to within around 1 kcal mol^{-1}.

Table 1 lists a series of reactions involving acetaldehyde, propanal, and butanal, with reaction enthalpies from the literature. No reactions were located for pentanal, hexanal, or

TABLE 3. Experimental and Computational Enthalpies of Formation for the Species Involved in Reactions A1, P1, and B1[a]

	$\Delta_f H°_{298}$ (experimental)	$\Delta_f H°_{298}$ (computational[b])
CH_3CH_2OH	**−56.23 ± 0.12**[26]	−55.6
$CH_3CH_2CH_2OH$	**−60.9 ± 1.1**[27]/−61.09 ± 0.31[14]/−61.85 ± 0.26[26]	−60.5
$CH_3CH{=}CHCH{=}O$	−24.03[24]/**−24.36 ± 0.12**[28]	−25.1

[a] The recommended enthalpy for each species is listed in bold. All values in kcal mol^{-1}. [b] Average of CBS-APNO, G3, and G3B3 isodesmic enthalpies. See Supporting Information for calculation details.

TABLE 4. Experimental Enthalpies of Formation for Acetaldehyde, Propanal, and Butanal[a]

	$\Delta_f H°_{298}$ (this study[b])	$\Delta_f H°_{298}$ (literature)
acetaldehyde	−39.72 ± 0.16	−39.70,[7] −40.80[10]
propanal	−45.18 ± 1.1	−44.46,[15] −45.09,[11] −45.55,[14] −45.9[13]
butanal	−49.27 ± 0.16	−48.85,[14] −50.61[10]

[a] All values in kcal mol^{-1}. [b] Calculated via thermodynamic cycles using known reaction and formation enthalpies.

heptanal. To evaluate the accuracy of the enthalpies provided in Table 1, each reaction enthalpy has been calculated with the G3, G3B3, and CBS-APNO methods, and the results are shown in Table 2. The difference between the experimental and computational reaction enthalpies for reactions A1, P1, and B1 is small enough for us to consider these experimental values to be correct. Accordingly, we will use only these three reactions in our thermodynamic analysis. For the remaining reactions, the difference between the experimental and computational values is close to the average error of the computational methods, and we are unable to judge whether the experimental values are correct.

The required enthalpies of formation for species in reactions A1, P1, and B1 are provided in Table 3. These values are compared to average computational values, calculated using the G3, G3B3, and CBS-APNO methods, with isodesmic work reactions (details are provided in Supporting Information). These enthalpy calculations should be accurate to below 1 kcal mol^{-1}, and can therefore help us select the most accurate experimental enthalpy. For methanol, the experimental and computational enthalpies agree to within the error of the computational value. For the remaining values, the enthalpy closest to our computational value has been selected for use in later calculations. The values listed in bold in Table 3 indicate those selected. While the enthalpy values selected for ethanol and propanol are in close agreement with the calculated values, that of crotonaldehyde ($CH_3CH{=}CHCH{=}O$) is not, with the experimental and computational values differing by ca. 1 kcal mol^{-1}. This is close to the largest error expected from our calculations, and we are therefore skeptical about the accuracy of the experimental enthalpy recommended for crotonaldehyde, and the enthalpy of formation of butanal calculated using this value.

Using the reaction and formation enthalpies recommended in Tables 1 and 3, the enthalpies of formation of acetaldehyde, propanal, and butanal have been calculated and are provided in Table 4, compared to previous experimental measurements. For acetaldehyde, reaction A1 gives an enthalpy of −39.72 ± 0.16 kcal mol^{-1}, which agrees well with the value evaluated by Pedley (−39.70 kcal mol^{-1}).[7] This supports the use of an enthalpy of −39.70 kcal mol^{-1} for acetaldehyde by da Silva et al.[11] in their isodesmic work reactions used to calculate the enthalpy of formation of formaldehyde. For propanal, we obtain an enthalpy of −45.18 ± 1.1 kcal mol^{-1} with reaction P1. This enthalpy is within error of the previous values of Buckley and Cox (−45.55 kcal mol^{-1})[14] and Wiberg (−45.09 kcal mol^{-1}).[10] Finally, for butanal, reaction B1 gives an enthalpy of formation of −49.27 ± 0.16 kcal mol^{-1}, which lies between the two previous enthalpy values reported in the literature (−50.61 kcal mol^{-1} by Wiberg[10] and −48.85 kcal mol^{-1} by Buckley and Cox[14]). The uncertainty in the enthalpy of formation of crotonaldehyde used to calculate the butanal formation enthalpy means that we are not able to identify which of the literature enthalpies is the more accurate.

Ab Initio Enthalpies of Formation. It is well-known that the use of isodesmic work reactions, where bonding regimes are conserved on both sides of the reaction, can result in considerable improvements in enthalpies of formation calculated by ab initio techniques. This improvement in accuracy is due to cancellation of systematic errors due to bonding, spin contamination, hindered internal rotation, basis set superposition, and other nonrandom error sources. It has been shown that the use of isodesmic work reactions with composite ab initio methods such as those of the Gaussian-*n* (G*n*) and complete basis set (CBS) varieties can lead to error reductions from around ±1 kcal mol^{-1} to ±0.5 kcal mol^{-1} or less.[11,17] Accordingly, we make use of isodesmic work reactions in order to accurately calculate the enthalpies of formation of the aldehydes.

When using isodesmic reactions for calculations on the aldehydes, the carbonyl C═O bond must be conserved on both sides of the reaction. As we do not wish to use other aldehydes as reference species in this study, we have made use of acetone and 2-butanone as the carbonyl reference species; both of these species have accurately measured enthalpies of formation. The remaining reference species in our isodesmic work reactions are aliphatic hydrocarbons and alcohols, which again have accurately known enthalpies of formation. Table 5 lists our isodesmic work reactions for the aldehydes acetaldehyde through heptanal. The reference enthalpies of formation for the isodesmic reactions are listed in Table 6 (unless already provided in Table 3).

The aldehyde enthalpies of formation have been calculated with the CBS-APNO, G3, and G3B3 theoretical methods for the isodesmic work reactions of Table 5. Hexanal and heptanal were too large to treat with the CBS-APNO method, and only G3 and G3B3 results were obtained. The computed reaction enthalpies for each of the isodesmic reactions (provided as Supporting Information) are all less than 11 kcal mol^{-1}, which indicates good cancellation of bond energy across the reaction, thus validating our selection of isodesmic work reactions. Table 7 lists the aldehyde enthalpies of formation calculated with each of the work reactions, along with average values for the three theoretical methods. The enthalpy values calculated by each of the three methods are within good agreement (0.3 kcal mol^{-1} or less).

Table 8 compares the best available experimental enthalpy values for each of the aldehydes and the average enthalpies calculated from the isodesmic reaction schemes. Also included in Table 8 are average enthalpies of formation calculated using atomization work reactions with the CBS-APNO, G3, and G3B3 theoretical methods, and the error relative to the experimental enthalpies. The experimental enthalpies of formation used in Table 8 are those calculated in this study for acetaldehyde,[34] propanal, and butanal, and the literature values for pentanal,[7] hexanal,[8] and heptanal.[9] The enthalpies of formation calculated using the isodesmic work reactions agree with the experimental

TABLE 5. Isodesmic Work Reaction Schemes for Acetaldehyde, Propanal, Butanal, Pentanal, and Hexanal

	Acetaldehyde
IA1	$CH_3CH{=}O + C_2H_6 \rightleftharpoons (CH_3)_2C{=}O + CH_4$
IA2	$CH_3CH{=}O + CH_3CH_2OH \rightleftharpoons (CH_3)_2C{=}O + CH_3OH$
IA3	$CH_3CH{=}O + C_3H_8 \rightleftharpoons (CH_3)_2C{=}O + C_2H_6$
IA4	$CH_3CH{=}O + CH_3CH_2CH_2OH \rightleftharpoons (CH_3)_2C{=}O + CH_3CH_2OH$
IA5	$CH_3CH{=}O + C_3H_8 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_4$
IA6	$CH_3CH{=}O + CH_3CH_2CH_2OH \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_3OH$
IA7	$CH_3CH{=}O + C_4H_{10} \rightleftharpoons CH_3C({=}O)CH_3CH_3 + C_2H_6$
	Propanal
IPr1	$CH_3CH_2CH{=}O \rightleftharpoons (CH_3)_2C{=}O$
IPr2	$CH_3CH_2CH{=}O + C_2H_6 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_4$
IPr3	$CH_3CH_2CH{=}O + CH_3CH_2OH \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_3OH$
IPr4	$CH_3CH_2CH{=}O + C_3H_8 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + C_2H_6$
IPr5	$CH_3CH_2CH{=}O + CH_3CH_2CH_2OH \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_3CH_2OH$
	Butanal
IB1	$CH_3CH_2CH_2CH{=}O \rightleftharpoons CH_3C({=}O)CH_2CH_3$
IB2	$CH_3CH_2CH_2CH{=}O + CH_4 \rightleftharpoons (CH_3)_2C{=}O + C_2H_6$
IB3	$CH_3CH_2CH_2CH{=}O + CH_3OH \rightleftharpoons (CH_3)_2C{=}O + CH_3CH_2OH$
IB4	$CH_3CH_2CH_2CH{=}O + C_2H_6 \rightleftharpoons (CH_3)_2C{=}O + C_3H_8$
IB5	$CH_3CH_2CH_2CH{=}O + CH_3CH_2OH \rightleftharpoons (CH_3)_2C{=}O + CH_3CH_2CH_2OH$
	Pentanal
IPe1	$CH_3CH_2CH_2CH_2CH{=}O + CH_4 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + C_2H_6$
IPe2	$CH_3CH_2CH_2CH_2CH{=}O + C_2H_6 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + C_3H_8$
IPe3	$CH_3CH_2CH_2CH_2CH{=}O + CH_3OH \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_3CH_2OH$
IPe4	$CH_3CH_2CH_2CH_2CH{=}O + CH_3CH_2OH \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_3CH_2CH_2OH$
IPe5	$CH_3CH_2CH_2CH_2CH{=}O + CH_4 \rightleftharpoons (CH_3)_2C{=}O + C_3H_8$
IPe6	$CH_3CH_2CH_2CH_2CH{=}O + CH_3OH \rightleftharpoons (CH_3)_2C{=}O + CH_3CH_2CH_2OH$
	Hexanal
IH1	$CH_3CH_2CH_2CH_2CH_2CH{=}O + CH_4 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + C_3H_8$
IH2	$CH_3CH_2CH_2CH_2CH_2CH{=}O + C_2H_6 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + C_4H_{10}$
IH3	$CH_3CH_2CH_2CH_2CH_2CH{=}O + CH_3OH \rightleftharpoons CH_3C({=}O)CH_2CH_3 + CH_3CH_2CH_2OH$
IH4	$CH_3CH_2CH_2CH_2CH_2CH{=}O + CH_4 \rightleftharpoons (CH_3)_2C{=}O + C_4H_{10}$
IH5	$CH_3CH_2CH_2CH_2CH_2CH{=}O + CH_3OH + C_2H_6 \rightleftharpoons (CH_3)_2C{=}O + CH_3CH_2CH_2OH + C_3H_8$
	Heptanal
IHep1	$CH_3CH_2CH_2CH_2CH_2CH{=}O + CH_4 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + C_4H_{10}$
IHep2	$CH_3CH_2CH_2CH_2CH_2CH{=}O + C_2H_6 \rightleftharpoons CH_3C({=}O)CH_2CH_3 + C_5H_{12}$
IHep3	$CH_3CH_2CH_2CH_2CH_2CH{=}O + CH_4 \rightleftharpoons (CH_3)_2C{=}O + C_5H_{12}$

TABLE 6. Experimental Enthalpies of Formation for Reference Species in the Isodesmic Reaction Schemes of Table 5

	$\Delta_f H^\circ_{298}$ (kcal mol^{-1})	ref
$(CH_3)_2C{=}O$	−52.23	10
$CH_3C({=}O)CH_2CH_3$	−57.02	29
CH_3OH	-48.00	30
CH_4	−17.89	31
C_2H_6	−20.04	32
C_3H_8	−25.02	32
C_4H_{10}	−30.03	32
C_5H_{12}	−35.08	33

values for acetaldehyde, propanal, pentanal, and hexanal to within ±0.5 kcal mol^{-1}, while the enthalpies calculated using atomization enthalpies agree to within ±0.8 kcal mol^{-1}. This confirms that our recommended experimental enthalpies for these four aldehydes are accurate to within the error of our calculations. The greatest difference between experimental and isodesmic enthalpies occurs with heptanal, where the error is 1.1 kcal mol^{-1}, and we recommend our enthalpy of −64.2 kcal mol^{-1} calculated using isodesmic work reactions as the best available value. For butanal, the isodesmic calculations yield an absolute error of 0.7 kcal mol^{-1}, while the atomization calculations yield an error of 0.8 kcal mol^{-1}. As discussed above, we feel that the enthalpy of formation of crotonaldehyde used in calculating the enthalpy of butanal is in error by as much as 1 kcal mol^{-1}, and this is supported by these results. Accordingly, we recommend the enthalpy of −50.0 kcal mol^{-1} as the best available estimate of the enthalpy of formation of butanal. Additionally, we assert that $\Delta_f H^\circ_{298} = -25.1$ kcal mol^{-1} for crotonaldehyde, from our isodesmic calculations.

Bond Dissociation Energies. Knowledge of the aldehyde BDEs is important in understanding their reaction chemistry in synthesis, combustion, and atmospheric processes. We have calculated the BDEs corresponding to homolytic C−H and C−C bond cleavage in formaldehyde, acetaldehyde, propanal, butanal, and pentanal from CBS-APNO 298 K enthalpies. BDEs for each of the aldehydes are listed in Table 9, along with literature values where available. In Table 9 we find that in all instances where literature BDEs exist there is good agreement with our calculated BDEs. In addition, enthalpies of formation for each of the radicals corresponding to C−H bond cleavage in the aldehydes have been calculated from the CBS-APNO BDEs, using the aldehyde enthalpies of formation recommended in this study. These enthalpies are reported in Table 10.

Table 9 shows that for each of the aldehydes the RC(═O)−H bond energy is between 88 and 90 kcal mol^{-1}, making this the weakest C−H bond in each of the aldehydes. The primary methyl (RCH_2−H) C−H bond energy steadily increases as the radical methyl carbon moves further away from the carbonyl group, and it peaks at around 103 kcal mol^{-1}, then plateaus lower for $CH_2(-H)CH_2CH_2CH{=}O$ and beyond. The plateau approximately corresponds to the C−H bond energy in saturated aliphatic hydrocarbons (ca. 101−102 kcal mol^{-1}), indicating that the carbonyl group exerts little influence past three carbon atoms. This is in accord with experimental results, where it has been found that HCO radical yields from aldehyde photolysis

TABLE 7. Enthalpy of Formation of Acetaldehyde, Propanal, Butanal, Pentanal, and Hexanal from Isodesmic Reactions with the CBS-APNO, G3, and G3B3 Theoretical Methods

	$\Delta_f H°_{298}$ (kcal mol^{-1})		
reaction	CBS-APNO	G3	G3B3
IA1	−39.9	−40.0	−40.1
IA2	−39.2	−39.5	−39.6
IA3	−39.8	−39.9	−40.0
IA4	−39.9	−40.1	−40.2
IA5	−39.4	−39.4	−39.6
IA6	−38.8	−39.1	−39.2
IA7	−39.3	−39.3	−39.5
av (acetaldehyde)	−39.5	−39.6	−39.7
IP1	−45.1	−45.3	−45.3
IP2	−44.7	−44.7	−44.9
IP3	−44.0	−44.2	−44.3
IP4	−44.5	−44.6	−44.8
IP5	−44.7	−44.8	−45.0
av (propanal)	−44.6	−44.7	−44.9
IB1	−49.4	−49.5	−49.7
IB2	−49.8	−50.1	−50.2
IB3	−50.5	−50.6	−50.7
IB4	−49.9	−50.2	−50.3
IB5	−49.8	−50.0	−50.1
av (butanal)	−49.9	−50.1	−50.2
IPe1	−53.6	−53.8	−53.9
IPe2	−53.7	−53.9	−54.0
IPe3	−54.3	−54.3	−54.5
IPe4	−53.6	−53.7	−53.8
IPe5	−54.1	−54.5	−54.5
IPe6	−54.7	−54.8	−54.8
av (pentanal)	−54.0	−54.2	−54.3
IH1		−58.9	−59.0
IH2		−58.9	−59.1
IH3		−59.2	−59.4
IH4		−59.5	−59.5
IH5		−59.9	−60.0
av (hexanal)		−59.3	−59.4
IHep1		−63.9	−64.0
IHep2		−64.0	−64.2
IHep3		−64.6	−64.6
av (heptanal)		−64.2	−64.3

TABLE 8. Average Enthalpies of Formation ($\Delta_f H°_{298}$'s) and Absolute Errors Relative to Experimental Enthalpies for the Aldehydes Calculated Using Isodesmic and Atomization Work Reactions with the CBS-APNO, G3, and G3B3 Theoretical Methods[a]

		isodesmic reaction		atomization reaction	
	exptl $\Delta_f H°_{298}$	$\Delta_f H°_{298}$	absolute error	$\Delta_f H°_{298}$	absolute error
acetaldehyde	**−39.72**[b]	−39.6	0.2	−39.8	0.1
propanal	**−45.18**[b]	−44.7	0.5	−45.2	0.0
butanal	−49.27[b]	**−50.0**	0.7	−50.2	0.8
pentanal	**−54.61**[7]	−54.1	0.5	−54.6	0.0
hexanal	**−59.37**[8]	−59.3	0.0	−58.6	0.8
heptanal	−63.1[9]	**−64.2**	1.1	−63.5	0.4

[a] All values in kcal mol^{-1}. The recommended enthalpy for each aldehyde is listed in bold. [b] This study.

TABLE 9. Bond Dissociation Energies (BDEs) for C−H and C−C Bonds in the Aldehydes

	BDE (kcal mol^{-1})	
	CBS-APNO	literature
Formaldehyde		
$H{-}CH{=}O$	88.2	88.2 ± 1.1[35]
Acetaldehyde		
$H{-}CH_2CH{=}O$	95.5	94.9 ± 0.5[36]
$CH_3C({=}O){-}H$	88.8	88.9 ± 0.7[35]
$CH_3{-}CH{=}O$	84.5	84.5 ± 1.0[35,37]
Propanal		
$H{-}CH_2CH_2CH{=}O$	102.4	
$CH_3C({-}H)HCH{=}O$	90.2	
$CH_3CH_2C({=}O){-}H$	89.3	
$CH_3{-}CH_2CH{=}O$	83.7	83.1 ± 1.2[36,37]
$CH_3CH_2{-}CH{=}O$	83.8	83.6 ± 1.6[35]
Butanal		
$H{-}CH_2CH_2CH_2CH{=}O$	102.2	
$CH_3CH({-}H)CH_2CH{=}O$	99.6	
$CH_3CH_2CH({-}H)CH{=}O$	90.6	
$CH_3CH_2CH_2C({=}O){-}H$	89.1	
$CH_3{-}CH_2CH_2CH{=}O$	90.1	
$CH_3CH_2{-}CH_2CH{=}O$	82.5	81.5 ± 1.2[35,36]
$CH_3CH_2CH_2{-}CH{=}O$	84.1	83.9 ± 1.5[35]
Pentanal		
$H{-}CH_2CH_2CH_2CH_2CH{=}O$	101.5	
$CH_3CH({-}H)CH_2CH_2CH{=}O$	98.6	
$CH_3CH_2CH({-}H)CH_2CH{=}O$	99.1	
$CH_3CH_2CH_2CH({-}H)CH{=}O$	89.5	
$CH_3CH_2CH_2CH_2C({=}O){-}H$	88.8	
$CH_3{-}CH_2CH_2CH_2CH{=}O$	89.4	
$CH_3CH_2{-}CH_2CH_2CH{=}O$	88.5	
$CH_3CH_2CH_2{-}CH_2CH{=}O$	82.3	81.6 ± 0.8[35,36]
$CH_3CH_2CH_2CH_2{-}CH{=}O$	83.4	

TABLE 10. Enthalpies of Formation of Radicals Corresponding to Loss of a H Atom in the Aldehydes

	$\Delta_f H°_{298}$ (kcal mol^{-1})
HCO	10.0
CH_2CHO	3.6
CH_3CO	−3.0
CH_2CH_2CHO	5.1
CH_3CHCHO	−7.1
CH_3CH_2CO	−8.0
$CH_2CH_2CH_2CHO$	0.1
CH_3CHCH_2CHO	−2.5
CH_3CH_2CHCHO	−11.5
$CH_3CH_2CH_2CO$	−13.0
$CH_2CH_2CH_2CH_2CHO$	−5.2
$CH_3CHCH_2CH_2CHO$	−8.1
$CH_3CH_2CHCH_2CHO$	−7.6
$CH_3CH_2CH_2CHCHO$	−17.2
$CH_3CH_2CH_2CH_2CO$	−18.3

do not vary with chain length for *n*-aldehydes larger than or equal to pentanal.[38]

The primary and secondary C−H BDEs are plotted in Figure 1, (i.e., $CH_2({-}H)R$ and $R'CH_2({-}H)R$). In the alkanes, primary C−H BDEs are ca. 101 kcal mol^{-1}, and secondary C−H BDEs are ca. 98.5 kcal mol^{-1}. Figure 1 demonstrates that the aldehyde C−H BDEs level off at around their alkane value when the hydrogen atom is removed from the fourth (or higher) carbon atom for primary and secondary C−H bonds. For both primary and secondary carbons, C−H bonds on the third carbon atom appear to be somewhat greater than those in the corresponding alkanes, indicating that the carbonyl group is inducing a small stabilizing effect in the parent aldehyde, which is not present in the radical, or a similar destabilizing effect in the radical which is not present in the aldehyde. A possible explanation for this stabilization in the parent aldehyde is the electrostatic interaction of the electronegative carbonyl group with the positive hydrogen dipole, as has been suggested by Wiberg and Martin.[39] Conversely, destabilization in the radical species could occur due to an unfavorable electrostatic interaction between the carbonyl group and the radical electron, or alternatively due to overlap between antibonding molecular orbital lobes on the carbonyl group and the radical carbon atom.

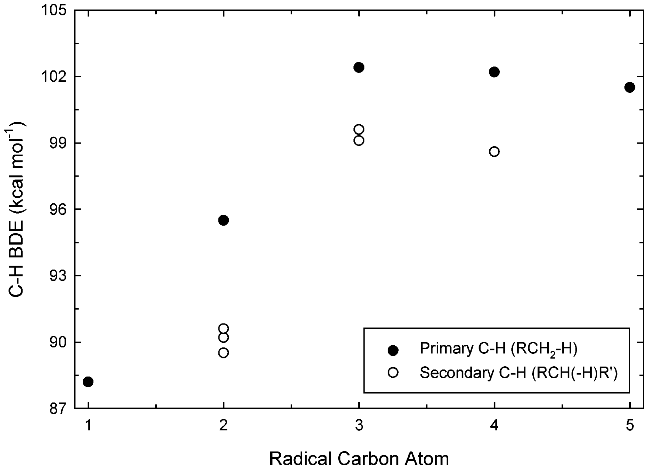

Figure 1. CBS-APNO bond dissociation energies (BDEs) for primary and secondary C—H bonds (i.e., RCH$_2$—H and RCH(—H)R′) in formaldehyde, acetaldehyde, propanal, butanal, and hexanal as a function of the position of the carbon atom. Numbering of the carbon atoms starts at the carbonyl carbon.

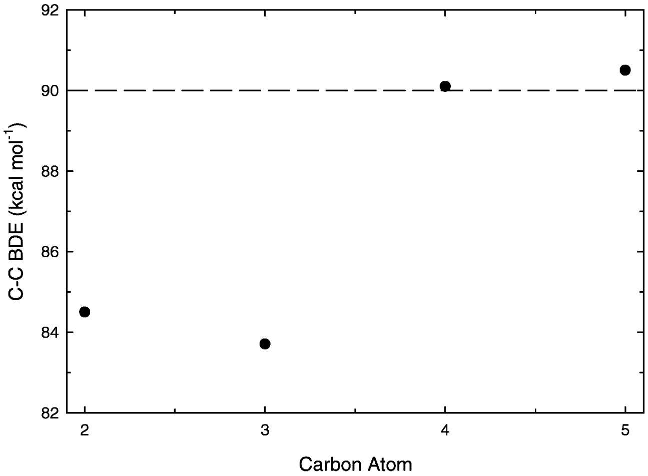

Figure 2. CBS-APNO bond dissociation energies (BDEs) of the terminal C—CH$_3$ bonds in acetaldehyde, propanal, butanal, and hexanal as a function of the position of the carbon atom. Numbering of the carbon atoms starts at the carbonyl carbon. Dashed line indicates approximate alkane C—CH$_3$ BDE.

Similar behavior to that of the C—H BDEs is witnessed with the C—C bond energies, where R—CH$_2$CH$_2$CH═O BDEs are all between 88 and 91 kcal mol^{-1}. Comparatively, C—C bond energies in saturated aliphatic hydrocarbons are around 87 to 90 kcal mol^{-1}. The weakest C—C bond in all of the aldehydes is the R—CH$_2$CH═O bond (ca. 82−83 kcal mol^{-1}), followed by the R—CH═O bond (ca. 84 kcal mol^{-1}). Cleavage of both these bonds results in the formation of resonantly stabilized radicals: the vinoxy radical (CH$_2$CH═O) and the formyl radical (CH═O). The lower BDE for formation of the vinoxy radical indicates that resonance stabilization in this radical is slightly larger than that in the formyl radical. We expect that both the vinoxy and formyl radicals will be important products of aldehyde combustion. It has been demonstrated that the equilibrium geometry of the CH$_2$CHO radical is closer to the formyl methyl structure (i.e., C$^•$H$_2$—CH═O) than the vinoxy structure (i.e., CH$_2$═CH—O$^•$), as the C═O double bond is ca. 10 kcal mol^{-1} stronger than the C═C double bond (see ref 4, and references therein).

Figure 2 illustrates the trends in R—C BDEs for the aldehydes as the bond being broken moves away from the carbonyl group. For the R—C bonds, the BDEs approach the alkane value for butanal and beyond. As discussed above, formation of the vinoxy radical by CH$_3$—CH$_2$CH═O bond cleavage is energetically more favorable than formyl radical formation by CH$_3$—CH═O bond cleavage. However, both BDEs are of comparable magnitude.

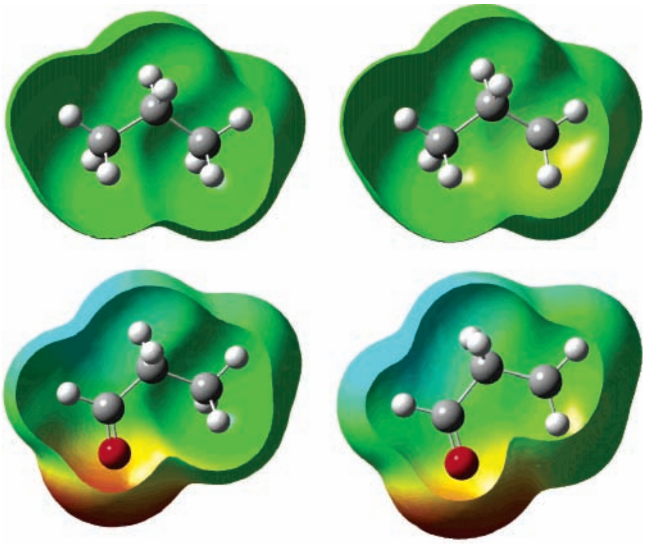

Figure 3. Cross-sections through the electrostatic potential surfaces, mapped onto the electron density, for propane, CH$_3$CH$_2$C$^•$H$_2$, C$^•$H$_2$-CH$_2$CH═O, and propanal (clockwise from top left). Charge range in all molecules is from −4.852 × 10^{-2} (red) to 4.852 × 10^{-2} (blue), where green represents neutral charge.

It has been shown by Wiberg and Martin that propanal, relative to propane, is stabilized by a dipole induced dipole−dipole interaction between the carbonyl and ethyl moieties.[39] Our calculations on RCHCH$_2$CHO radicals (where R = H, CH$_3$, or CH$_3$CH$_2$) reveal BDEs for formation of these radicals that are between 0.6 and 1.4 kcal mol^{-1} more stable than for the corresponding alkanes. The CH$_3$—CH$_2$CH$_2$CHO and CH$_3$-CH$_2$—CH$_2$CH$_2$CHO BDEs are calculated to be 90.1 and 88.5 kcal mol^{-1}, while the CH$_3$—CH$_2$CH$_2$CH$_3$ and CH$_3$CH$_2$—CH$_2$-CH$_2$CH$_3$ BDEs are 88.8 and 87.4 kcal mol^{-1}. Furthermore, the BDEs for H—CH$_2$CH$_2$CHO, CH$_3$CH(—H)CH$_2$CHO, and CH$_3$-CH$_2$CH(—H)CH$_2$CHO are 102.4, 99.6, and 99.1 kcal mol^{-1}, while the analogous alkane values are 101 kcal mol^{-1} for primary C—H bonds and 98.5 kcal mol^{-1} for secondary C—H bonds. On average, the C—H and C—C BDEs on the third carbon atom in the aldehydes are 1.1 kcal mol^{-1} weaker than those in similar alkane molecules. As discussed above, this lowering of the bond dissociation energies could be a result of stabilization in the parent aldehydes or destabilization in the RCHCH$_2$CHO radicals.

To explore the possibility that an electrostatic interaction is stabilizing the aldehydes larger than acetaldehyde, versus the RCHCH$_2$CHO radicals, we have mapped the electrostatic potential onto the total electron density for propanal and its primary radical C$^•$H$_2$CH$_2$CH═O. Cross-sections through these electrostatic potential surfaces are shown in Figure 3, with comparison to similar diagrams for propane and its primary radical C$^•$H$_2$CH$_2$CH$_3$. The figure illustrates that propane is essentially neutrally charged, relative to the other molecules, while the strong negative charge on the carbonyl group in propanal results in the polarization of this molecule's CH$_3$CH$_2$ moiety. This mechanism of polarization appears to be operating to a similar effect in the C$^•$H$_2$CH$_2$CH═O radical.

The dipole induced dipole−dipole interaction between the carbonyl group and the ethyl group in propanol, as proposed

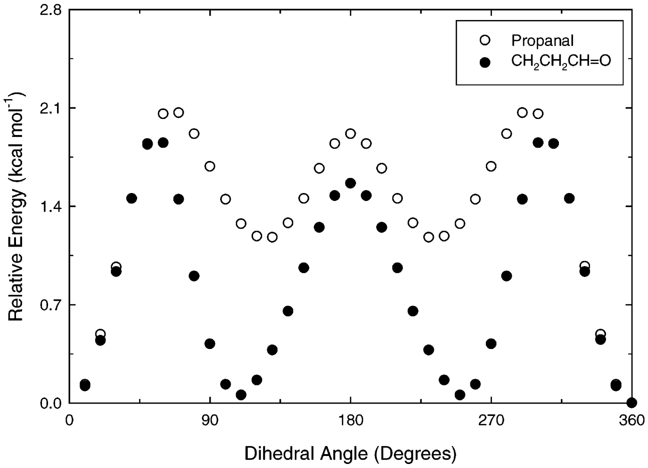

Figure 4. Potential energy profile for the CC—CO internal rotors in propanal and the $CH_2CH_2CH{=}O$ radical, calculated at the TPSSh/6-31G(d) level of theory.

by Wiberg and Martin,[39] is examined here through scans of the CC—CO internal rotor in both propanal and the $C^\bullet H_2CH_2CH{=}O$ radical, as shown in Figure 4. Calculations were performed at the TPSSh/6-31G(d) level,[40] as the TPSSh density functional provides a better account of long-range nonbonded intramolecular interactions than many other DFT methods, including the popular B3LYP method. In Figure 4, we find that the internal barrier to rotation in both molecules is essentially the same, at about 2 kcal mol^{-1}. This agrees relatively well with prior calculations[39] and experimental measurements[41] of the propanal CH_3CH_2—$CH_2CH{=}O$ internal rotor potential. For propanal, the synperiplanar conformation is more stable than the antiperiplanar conformation by around 1.2 kcal mol^{-1}, which approximately corresponds to the degree of dipole-induced stabilization. However, for the $C^\bullet H_2CH_2CH{=}O$ radical we find that the syn and anti conformers are of similar energy. This is thought to indicate that the dipole induced dipole—dipole interaction which stabilizes the synperiplanar conformation of propanal is lost in the $C^\bullet H_2CH_2CH{=}O$ radical, which results in the observed 1—2 kcal mol^{-1} increase in energy for the aldehyde C—H and C—C bonds that result in $RC^\bullet HCH_2CH{=}O$ radical formation.

Our BDE calculations indicate that the reactions of the aldehydes in thermal systems should preferentially result in formation of the formyl ($RCH_2C^\bullet{=}O$) and vinoxy ($RC^\bullet H$—$CH{=}O$) radicals. These two radicals are common combustion intermediates, and their further reaction pathways are important. The vinoxy radical is known to unimolecularly dissociate to give either CH_3 and CO or ketene and H.[36,42,43] The formation of CH_3 is important, as methyl radicals abstract hydrogen atoms from hydrocarbons to form methane.[44] The vinoxy radical will also react with molecular oxygen during combustion and in the atmosphere, yielding products such as CO, HCO, OH, and the peroxy radical.[45,46] The formyl radical rapidly dissociates to give H + CO, and undergoes hydrogen abstraction with the radical pool to give CO and products such as H_2, H_2O, and HO_2.[47−49] Formaldehyde is also a minor reaction product of vinoxy radical oxidation.[50,51]

Acetaldehyde is also capable of forming the vinoxy radical, by dissociation of the H—$CH_2CH{=}O$ bond. However, cleavage of this bond is less favorable than dissociation of the $CH_3C({=}O)$—H bond by almost 7 kcal mol^{-1}, with respective BDEs of 95.5 and 88.8 kcal mol^{-1}. Taylor et al.[52] studied the reaction of acetaldehyde with OH, and found that abstraction of the weaker acetyl hydrogen atom is the dominant reaction pathway at temperatures of 600 K or below, while H abstraction from the methyl group, giving the vinoxy radical, is more important at higher temperatures, as entropy begins to dominate. We can expect the vinoxy radical to undergo an intramolecular hydrogen shift reaction to produce the acetyl radical, with the reaction being exothermic by around 7 kcal mol^{-1}. The activation energy for the conversion of the vinoxy radical to the acetyl radical has been calculated as 40 kcal mol^{-1} at the CBS-APNO level.[36] The acetyl radical readily undergoes decomposition to CH_3 and CO,[36,43] with an activation energy of around 17 kcal mol^{-1}.[36] The acetyl radical will also undergo β-scission to ketene + H, or hydrogen abstraction by available radicals ($X^\bullet$) to from ketene + XH.[36] The acetyl radical can react with O_2, resulting in products such as formaldehyde + HO_2 and the $C^\bullet H_2CO_2^\bullet$ diradical + OH, as well as the stabilized acetyl-peroxy adduct ($CH_3C({=}O)OO^\bullet$) at low temperatures.[53,54]

TABLE 11. Calculated Lengths of the C═O, C—CO, and H—CO Bonds in the Aldehydes at the QCISD/6-311G(d,p) Level of Theory

	C═O (Å)	C—CO (Å)	H—CO (Å)
formaldehyde	1.2062		1.1082
acetaldehyde	1.2079	1.5132	1.1122
propanal	1.2086	1.5166	1.1125
butanal	1.2088	1.5148	1.1138
pentanal	1.2087	1.5148	1.1138
hexanal	1.2088	1.5148	1.1139
heptanal	1.2089	1.5148	1.1139

TABLE 12. Calculated Lengths of the C═O, C—CO, and H—CO Bonds in the Radicals Corresponding to Loss of a Hydrogen Atom from the Aldehydes Calculated at the QCISD/6-311G(d,p) Level of Theory

	C═O (Å)	C—CO (Å)	H—CO (Å)
	—C$^\bullet$O		
HCO	1.1805		1.1257
$CH_3C{=}O$	1.1842	1.5261	
$CH_3CH_2C{=}O$	1.1854	1.5315	
$CH_3CH_2CH_2C{=}O$	1.1857	1.5306	
$CH_3CH_2CH_2CH_2C{=}O$	1.1857	1.5308	
	—C$^\bullet$CO		
$CH_2CH{=}O$	1.2311	1.4408	1.1062
$CH_3CHCH{=}O$	1.2314	1.4435	1.1063
$CH_3CH_2CHCH{=}O$	1.2318	1.4437	1.1065
$CH_3CH_2CH_2CHCH{=}O$	1.2318	1.4438	1.1066
	—C$^\bullet$CCO		
$CH_2CH_2CH{=}O$	1.2062	1.5306	1.1128
$CH_3CHCH_2CH{=}O$	1.2078	1.5191	1.1119
$CH_3CH_2CHCH_2CH{=}O$	1.2079	1.5192	1.1119
	—C$^\bullet$CCCO		
$CH_2CH_2CH_2CH{=}O$	1.2090	1.5160	1.1122
$CH_3CHCH_2CH_2CH{=}O$	1.2091	1.5158	1.1124
	—C$^\bullet$CCCCO		
$CH_2CH_2CH_2CH_2CH{=}O$	1.2089	1.5165	1.1124

Molecular Structures. Table 11 gives the C═O, C—CO, and H—CO bond lengths in the aldehydes up to heptanal, calculated at the QCISD/6-311G(d,p) level of theory. We find that the geometry of the R—CH═O moiety is essentially unchanged for propanal through heptanal, corresponding to those aldehydes that are stabilized in the synperiplanar conformation. Compared to formaldehyde and acetaldehyde, these aldehydes show a slightly longer C═O bond of ca. 1.209 Å, an increase of 0.001 to 0.002 Å.

Table 12 lists bond lengths in the radicals corresponding to loss of a hydrogen atom from the aldehydes up to pentanal. For the species with the radical electron at the fourth and fifth carbon atoms (i.e., —C$^\bullet$CCCO and —C$^\bullet$CCCCO) we find that the geometrical parameters of the carbonyl group are very similar to those in the parent aldehydes, with only a small lengthening (0.001−0.002 Å) of the C═O bond. When the radical is on the third carbon (—C•CCO) we find a significant lengthening of the C—CO bond (0.004—0.014 Å), with contraction of the C═O bond (0.0008—0.0024 Å). This effect is most pronounced in the $C^{\bullet}H_2CH_2CH{=}O$ radical. Lengthening of the C—CO bond and shortening of the C═O bond is in accord with our earlier finding that the interaction stabilizing the aldehydes (larger than acetaldehyde) in the synperiplanar conformation is largely destroyed in the $RC^{\bullet}HCH_2CH{=}O$ radicals.

While the geometrical changes found for the $RC^{\bullet}HCH_2CH{=}O$ radicals are significant, the greatest changes occur when the radical electron is on either the $C^{\bullet}{=}O$ or the $C^{\bullet}C{=}O$ carbon atom. For species with the radical electron on the carbonyl carbon we find that the C═O bond is shorter than that in the parent aldehydes (by ca. 0.025 Å), while the C—CO (and H—CO) bond is longer (ca. 0.015 Å). This is a result of resonance stabilization in these radicals between the $C{-}C^{\bullet}{=}O$ and $C{-}C^{\oplus}{=}O^{\ominus\bullet}$ molecular structures, where attraction between the formal charges in the minor resonance structure results in contraction of the C═O bond, with a commensurate lengthening of the carbon—carbon bond. When the aldehydes lose a hydrogen from the carbon atom bonded to the carbonyl-carbon, the C═O bond lengthens by ca. 0.025 Å and the C−CO bond shortens by ca. 0.072 Å. We can attribute this to resonance stabilization between the $C{=}CH{-}O^{\bullet}$ and $C^{\bullet}{-}CH{=}O$ structures. These observations agree with our bond energy calculations, where the weakest C—H bonds in the aldehydes were identified as those on the carbonyl carbon and the adjacent carbon atom, due to the significant degree of resonance stabilization.

Group Additivity. Group additivity is a technique for accurately estimating thermochemical parameters based upon the contributions of individual molecular groups. The group additivity components for formaldehyde, acetaldehyde, and propanal are listed below. For aldehydes larger than propanal, the $C/C_2/H_2$ group would be added for each additional CH_2 group.

$$\text{formaldehyde} = CO/H_2$$

$$\text{acetaldehyde} = CO/C/H + C/CO/H_3$$

$$\text{propanal} = CO/C/H + C/C/CO/H_2 + C/C/H_3$$

While the $C/C/H_3$ and $C/C_2/H_2$ group enthalpies are precisely known (−10.00 and −5.00 kcal mol^{-1})[55] from the thermochemical property data of the alkanes, there is greater uncertainty for many of the carbon−hydrogen−oxygen group enthalpies. This includes the CO/H_2, CO/C/H, $C/CO/H_3$, and $C/C/CO/H_2$ groups, which are all present in the aldehydes. From the enthalpy of formation of formaldehyde,[11] the CO/H_2 group is −26.05 kcal mol^{-1}. This agrees with the value of −26.0 kcal mol^{-1} determined by Benson.[56] Using the enthalpies of formation recommended in this study for the aldehydes up to heptanal, and the literature group values for $C/C/H_3$ and $C/C_2/H_2$, the enthalpies of the CO/C/H, $C/CO/H_3$, and $C/C/\ CO/H_2$ groups have been determined as −29.39, −10.33, and −5.22 kcal mol^{-1}, respectively. These values were obtained by numerically fitting the unknown group values using a least-squares procedure. The group additivity values obtained by this procedure reproduce the recommended enthalpies of the six aldehydes with an average error of 0.3 kcal mol^{-1}.

The group additivity values calculated in this study are compared to the literature values of Benson[56] and Cohen[55] in Table 13. The CO/C/H enthalpy value of −29.47 kcal mol^{-1} agrees with the value recommended by Cohen (−29.4 kcal mol^{-1})[55] but is slightly smaller than the value of Benson (−29.10 kcal mol^{-1}),[56] while the $C/C/CO/H_2$ group value of −5.26 kcal mol^{-1} is in agreement with the group value of −5.2 kcal mol^{-1} recommended by both Benson[56] and Cohen.[55] The $C/CO/H_3$ group value determined here (−10.31 kcal mol^{-1}) is somewhat smaller than the values recommended by Benson[56] and Cohen[55] (−10.08 and −10.0 kcal mol^{-1}, respectively) but is still in relatively good agreement.

TABLE 13. Group Additivity Enthalpy Values

group	group additivity enthalpy value (kcal mol^{-1})		
	this study	Benson[56]	Cohen[55]
CO/C/H	−29.47	−29.1	−29.4
$C/CO/H_3$	−10.31	−10.08	−10
$C/C/CO/H_2$	−5.26	−5.2	−5.2

The additivity groups for the *n*-aldehydes larger than propanal only differ by the number of $C/C_2/H_2$ groups, and their enthalpies of formation should therefore decrease by ca. 5 kcal mol^{-1} for every additional CH_2 group. Using the recommended enthalpies of formation from this study, the enthalpy differences in going from propanal to butanal, butanal to pentanal, pentanal to hexanal, and hexanal to heptanal are −4.8, −4.6, −4.8, and −4.8 kcal mol^{-1}. These values are all in good agreement with each other and compare well with the literature value for the alkanes (−5.00 kcal mol^{-1}). For comparison, we note that use of the experimental enthalpies reported in Table 8, including the values for butanal and heptanal, then enthalpy differences between aldehydes corresponding to a CH_2 group, span a range of −3.7 to −5.3 kcal mol^{-1}. This provides further evidence that the enthalpies for butanal and heptanal calculated using isodesmic work reactions are correct.

There does appear to be a small systematic difference between the enthalpy increment of −4.8 kcal mol^{-1} found for the aldehydes and the value of −5.00 kcal mol^{-1} reported for the alkanes. Cohen and Benson[57] discuss the $C/C_2/H_2$ group additivity value, and note that a value of −5.00 kcal mol^{-1} is obtained with the alkanes up to C_{18}. They also note that when thermochemical values for the alkenes are included this value drops to −4.95 kcal mol^{-1}. Cohen and Benson[57] were unable to definitively rule between these two values, and raised the possibility that the $C/C/H_2$ group value may vary depending on the functional groups present in a molecule. It is not clear whether the $C/C_2/H_2$ group increment of −4.8 kcal mol^{-1} found in this study is the result of a small error in our group value, or if it is indicative of a systematic effect propagated through the small aldehydes in this study, by the carbonyl group. If the change results from the carbonyl moiety, it may be due to polarization of the alkane tail, as seen in Figure 3 for propanal.

Conclusion

Accurate experimental enthalpies of formation for acetaldehyde, propanal, and butanal have been determined from thermodynamic cycles making use of existing enthalpies of reaction and enthalpies of formation. Ab initio calculations confirmed all experimental reference enthalpies to be accurate to within around ±1 kcal mol^{-1}. This approach provided enthalpies of −39.72 kcal mol^{-1} for acetaldehyde, −45.18 kcal mol^{-1} for propanal, and −49.27 kcal mol^{-1} for butanal. The enthalpies of formation of acetaldehyde, propanal, butanal, pentanal, hexanal, and heptanal were calculated as −39.6, −44.7, −50.0, −54.1, −59.3, and −64.2 kcal mol^{-1}, respectively, using the ab initio methods CBS-APNO, G3, and G3B3, with isodesmic work reactions used to minimize calculation errors. Bond dissociation energies (BDEs) for all $C-C$ and $C-H$ bonds in formaldehyde, acetaldehyde, propanal, butanal, and pentanal were calculated using the CBS-APNO theoretical method. For all aldehydes larger than acetaldehyde, the $R-CH_2CH=O$ bond is the weakest of all bonds, due to formation of the resonantly stabilized vinoxy radical. It is proposed that the vinoxy radical, in addition to the more commonly considered formyl and acetyl radicals, are important products of aldehyde combustion and oxidation. Electrostatic potential surfaces and internal rotor profiles are used to examine the dipole induced dipole−dipole stabilization of the synperiplanar conformation of propanal, and the destruction of this dipole interaction in $RC^{\bullet}HCH_2CH=O$ radicals is found to result in a decrease in the aldehyde $C-H$ and $C-C$ bonds leading to $RC^{\bullet}HCH_2CH=O$ radical formation.

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Supporting Information Available: Molecular geometries for the aldehydes at the HF/6-31G(d), MP2/6-31G(d), B3LYP/6-31G(d), HF/6-311G(d,p), and QCISD/6-311G(d,p) theoretical methods. Molecular enthalpies for all species at the G3, G3B3, and CBS-APNO level. Enthalpy corrections due to hindered internal rotation. Reaction enthalpies for isodesmic work reactions calculated at the G3, G3B3, and CBS-APNO levels. Isodesmic calculations used to determine enthalpies of formation of ethanol, propanol and crotonaldehyde. This material is available free of charage via the Internet at http://pubs.acs.org.

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(34) Since submitting this manuscript, we have performed a W1 atomization calculation on acetaldehyde. This calculation found the acetaldehyde enthalpy to be -40.50 kcal mol^{-1}, which is in close agreement with the CBS-QB3 calculation of Carstenson et al.[12] The W1 value also supports the experimental value of -40.8 kcal mol^{-1} [10] as opposed to the experimental value of -39.7 kcal mol^{-1},[7] which our calculations agree with. It is likely that the true enthalpy for acetaldehyde lies between the two reported experimental values.

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