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Formation Enthalpies and Bond Dissociation Energies of Alkylfurans. The Strongest C−X Bonds Known?

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Enthalpies of formation, ΔH_f(298.15 K), of 2-methyl-, 3-methyl-, 2-ethyl-, 2-vinyl-, 2,3-dimethyl-, 2,4-dimethyl-, and 3,4-dimethylfurans are computed with three compound quantum chemical methods, CBS-QB3, CBS-APNO, and G3, via a number of isodesmic reactions. We show that previously experimentally determined enthalpies of formation of furan itself, 2,5-dimethyl-, 2-*tert*-butyl-, and 2,5-di-*tert*-butylfurans are self-consistent but that for 2-vinylfuran is most probably in error. The formation enthalpies of over 20 furyl and furfuryl radicals have also been determined and consequently the bond dissociation energies of a number of C−H, C−CH_3, C−F, C−Cl, and C−OH bonds. The ring-carbon−H bonds in alkylfurans are much stronger than previously thought and are among the strongest ever C−H bonds recorded exceeding 500 kJ mol^{-1}. The relative thermodynamic instability of the various furyl radicals means that bonds to methyl, fluorine, and chlorine are also unusually strong. This is as a consequence of the inability of the radical to effectively delocalize the unpaired electron and the geometrical inflexibility of the five-membered heterocyclic ring. By way of contrast the furfuryl radicals are more stable than similar benzyl radicals which results in weaker side-chain C−H bonds than the corresponding toluene derivatives (although stronger than the corresponding cyclopentadiene analogue). These results have implications for the construction of detailed chemical kinetic models to account for the thermal decomposition and oxidation of alkylfurans either in engines or in the atmosphere.

Introduction

The synthesis of new biofuels by second generation methods of production from biomass is one of the most exciting developments in recent times, transforming abundant renewable resources, but not crops destined for human consumption, into liquid transport fuels.[1,2] Thus Román-Leshkov and colleagues[3] have explored a catalytic strategy—acid-catalyzed dehydration of fructose followed by copper−ruthenium catalyzed hydrogenolysis of the resulting 5-hydroxymethylfurfural—to yield inter alia 2,5-dimethylfuran. While Atsumi et al.[4] have used the manipulation of biological systems or *metabolic engineering* to produce higher alcohols such as 1-butanol. These second-generation methods of production are very interesting, but the question that must be asked is just how good are these next-generation biofuels? How quickly do they ignite? What intermediates are liable to be formed during the combustion process? Do they represent a threat to human health, to the atmosphere, or the hydrosphere?

Detailed chemical kinetic models exist to describe the combustion of hydrocarbons,[5] but these are largely absent for oxygenated species such as furans and higher alcohols. In order to frame suitable mechanisms, elucidation of the enthalpies of formation and bond dissociation energies is crucial for successful simulations.

Experimental measurements of bond dissociation energies can be difficult with the result that only some 7000 out of over 30 million known compounds have ever been so determined.[6] This applies to the alkylfurans which renders kinetic analysis of the thermal decomposition pathways[7−9] and hydrogen-atom abstraction channels quite difficult to frame. Thus, for example, a study[10] of the thermal reactions of 2,5-dimethylfuran, a necessary but not sufficient prequel to work on the combustion chemistry of this compound, had to rely on estimates of the C−H and C−C bond dissociation energies. In *this work* we use high-level computational methods to circumvent this deficit and provide reliable and self-consistent values.

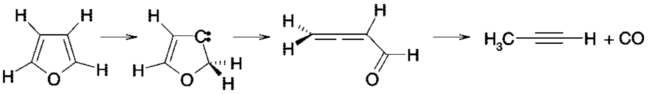

Figure 1. One channel in the unimolecular decomposition of furan.[16]

As regards experimental measurements Verevkin and Welle[11] have determined enthalpies of formation of 2,5-dimethyl-, 2-*tert*-butyl-, and 2,5-di-*tert*-butylfurans, 2-vinylfuran was measured by Landrieu et al.,[12] while furan itself was determined by Guthrie et al.[13] and more recently by Zaheeruddin and Lodhi.[14]

Note that theoretical investigations of the unimolecular decomposition channels of furans[15,9] are likely to be quite challenging; for example, Liu et al. explored the thermal decomposition of furan at modest levels of theory (geometry optimization at B3LYP/6-21G** followed by single point energies up to QCISD(T)/6-211G**) and proposed a complex rearrangement scheme, Figure 1, yielding methylacetylene and carbon monoxide—major products found in the thermal decomposition of furan.[16]

Both 2,5-dimethylfuran and 2-methylfuran have been identified as biomarkers of recent exposure to cigarette smoke in exhaled air;[17] the aromatic furan ring is found in a wide range of aroma chemicals[18] with the dimethyl compound responsible for the perceived off-odor and off-flavors in liquid sugars.[19]

Furans are emitted into the atmosphere from burning fossil fuels, waste, and biomass[20] and can be formed from isoprene by reaction

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TABLE 1: Enthalpies at 298.15 K of 2-Methylfuran Target (O = oxirane, MO = methyloxirane)

	2MF	+	2MF	=	F	+	DMF	ΔH_r/au	ΔH_r/kJ mol^{-1}	mean	2σ
QB3	−268.871675		−268.871675		−229.638424		−308.104741	0.000185	0.49		
APNO	−269.233241		−269.233241		−229.941643		−308.524781	0.000058	0.15	0.42	0.48
G3	−269.133826		−269.133826		−229.855244		−308.412173	0.000235	0.62		
	−81.62				−34.7		−128.13				
	±0.65				±0.7		±0.98				
	2MF	+	ethene	=	F	+	propene	ΔH_r/au	ΔH_r/kJ mol^{-1}	mean	2σ
QB3	−268.871675		−78.412647		−229.638424		−117.641178	0.004720	12.39		
APNO	−269.233241		−78.528219		−229.941643		−117.815456	0.004361	11.45	12.26	1.51
G3	−269.133826		−78.503424		−229.855244		−117.777077	0.004929	12.94		
	−79.29		52.57		−34.7		20.24				
	±1.73		±0.21		±0.7		±0.41				
	2MF	+	O	=	F	+	MO	ΔH_r/au	ΔH_r/kJ mol^{-1}	mean	2σ
QB3	−268.871675		−153.535193		−229.638424		−192.767510	0.000934	2.45		
APNO	−269.233241		−153.723030		−229.941643		−193.013874	0.000754	1.98	2.27	0.50
G3	−269.133826		−153.666476		−229.855244		−192.944156	0.000902	2.37		
	−79.01		−52.64		−34.7		−94.68				
	±1.21		±0.6		±0.7		±0.6				
	2MF	+	neopentane	=	TBF	+	ethane	ΔH_r/au	ΔH_r/kJ mol^{-1}	mean	2σ
QB3	−268.871675		−197.307476		−386.552713		−79.626134	0.000304	0.80		
APNO	−269.233241		−197.600105		−387.089457		−79.743563	0.000326	0.86	0.47	1.23
G3	−269.133826		−197.535838		−386.950842		−79.718911	−0.000089	−0.23		
	−80.16		−167.9		−163.8		−83.8				
	±1.59		±0.63		±0.76		±0.2				

TABLE 2: Calculated Formation Enthalpies/kJ mol^{-1}

furan	ΔH_f(298.15 K)
2-methyl	−80.8 ± 0.5
3-methyl	−69.5 ± 0.5
2-vinyl	13.7 ± 0.6
2-ethyl	−101.2 ± 0.7
2,3-dimethyl	−116.5 ± 1.1
2,4-dimethyl	−117.6 ± 1.0
3,4-dimethyl	−107.6 ± 1.0

TABLE 3: Formation Enthalpies of Reference Species/kJ mol^{-1}

species	ΔH_f(298.15 K)	species	ΔH_f(298.15 K)
ethane	−83.78 ± 0.20[54]	propane	−104.7 ± 0.6[54]
ethene	52.57 ± 0.21[54]	propene	20.24 ± 0.41[54]
benzene	82.88 ± 0.26[54]	vinylbenzene	146.9 ± 1.0[55]
toluene	50.40 ± 0.63[54]	ethylbenzene	29.8 ± 0.84[56]
butadiene	108.4 ± 0.79[57]	neopentane	−167.9 ± 0.63[58]
oxirane	−52.63 ± 0.63[59]	methyloxirane	−94.68 ± 0.63[60]

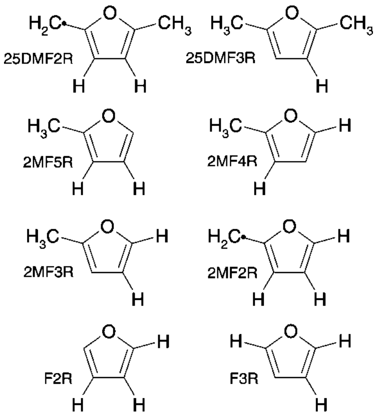

Figure 2. Radical nomenclature.

TABLE 4: ⟨S^2⟩

method	phenyl	vinyl	2MF4R	benzyl	allyl	3MF3R
CBS-QB3	0.757	0.760	0.757	0.781	0.779	0.773
CBS-APNO	1.403	0.990	1.042	1.370	0.965	1.061
G3	1.430	1.015	1.066	1.391	0.973	1.078

with hydroxyl radical.[21] Subsequent reaction with both hydroxyl and nitrate radicals and chlorine and bromine atoms play a role in their depletion.[22−25] The reactivity of $^{\bullet}$OH toward furans increases with increasing alkylation 2,5-dimethyl > 2-ethyl > methyl > furan and varies with position on the ring so that the 3-methyl isomer is more readily attacked than 2-methylfuran.[26] Much the same trends are seen in reactions with the $^{\bullet}NO_3$ radical except that for the dimethyl compounds the 2,5-, 2,3-, and 2,4-isomers exhibit similar reactivities and the tetramethyl-substituted furan is the most reactive of all.[22] It is likely that the atmospheric reactions with $^{\bullet}$OH/$^{\bullet}NO_3$ radicals and Cl/Br atoms proceeds initially by addition rather than abstraction as evidenced by theoretical calculations by Zhang et al. for $^{\bullet}$OH + 3-methylfuran.[27] They show that H-abstraction of ring hydrogens have barriers of 40−50 kJ mol^{-1}, abstraction from the methyl group has a barrier height of 12 kJ mol^{-1} whereas association−elimination is barrierless and is the dominant reaction path.

The same reactivity is shown at high temperatures; thus Grela et al.[9] showed that 2,5-dimethyl decomposes faster at approximately 1100 K in a low-pressure flow reactor than 2-methyl which in turn reacts faster than furan itself—findings subsequently confirmed by Lifshitz et al. in shock tube experiments.[10] We have shown, in high-temperature autoignition measurements behind reflected shock waves, that under identical conditions of temperature, pressure, and, fuel and oxygen concentrations 2,5-dimethylfuran is much harder to ignite than 1-butanol which in turn is harder to ignite than ethanol.[28]

Results

For the calculation of molecular energies we have employed composite methods which have a sequence of predefined computations and which are comprised of computationally inexpensive optimization and frequency calculations with more expensive single point energy determinations. The complete

TABLE 5: Calculated Enthalpies of Formation, ΔH_f(298.15 K)/kJ mol^{-1}, of Radicals via Isodesmic Reactions; Key Radicals in Bold

species	ΔH_f	species	ΔH_f
	Furyl Radicals		
25DMF3R	157.2 ± 5.5	34DMF2R	177.4 ± 5.9
24DMF3R	167.7 ± 5.5	24DMF5R	168.5 ± 5.7
23DMF4R	168.2 ± 5.5	23DMF5R	167.6 ± 5.8
2MF3R	205.7 ± 5.6	2MF4R	204.9 ± 5.7
2MF5R	204.9 ± 5.7	3MF2R	217.3 ± 5.8
3MF4R	216.3 ± 5.7	3MF5R	214.9 ± 5.7
F2R	251.9 ± 5.5	**F3R**	252.3 ± 5.4
	Furfuryl Radicals		
25DMF2R	11.6 ± 5.8	34DMF3R	50.2 ± 6.0
24DMF2R	24.3 ± 5.8	24DMF4R	40.0 ± 6.2
23DMF2R	22.2 ± 5.8	23DMF3R	40.3 ± 5.9
2MF2R	62.1 ± 5.2	3MF3R	90.4 ± 5.3

TABLE 6: Bond Dissociation Energies of Furfuryl Species at 298.15 K/kJ mol^{-1}

species	D(C−H)	species	D(C−H)
25DMF2R−H	357.8 ± 5.9	34DMF3R−H	375.8 ± 6.0
24DMF2R−H	359.9 ± 5.9	24DMF4R−H	375.6 ± 6.3
23DMF2R−H	356.7 ± 5.9	23DMF3R−H	374.8 ± 6.0
2MF2R−H	360.9 ± 5.2	3MF3R−H	377.9 ± 5.3

TABLE 7: Bond Dissociation Energies at 298.15 K/kJ mol^{-1}

species	D(C−CH_3)	species	D(C−CH_3)
2MF5R	479.8 ± 5.8	3MF4R	470.6 ± 5.7
3MF2R	480.5 ± 5.9	2MF3R	468.9 ± 5.7
3MF5R	479.2 ± 5.8	2MF4R	469.2 ± 5.8
F2R	479.4 ± 5.6	F3R	468.5 ± 5.5

TABLE 8: Bond Dissociation Energies at 298.15 K/kJ mol^{-1}

species	D(ring C−H)	species	D(ring C−H)
25DMF3R−H	503.3 ± 5.6	34DMF2R−H	503.0 ± 5.9
24DMF3R−H	503.3 ± 5.6	24DMF5R−H	504.0 ± 5.8
23DMF4R−H	502.7 ± 5.6	23DMF5R−H	502.1 ± 5.9
2MF3R−H	504.5 ± 5.7	3MF2R−H	504.8 ± 5.8
2MF4R−H	503.7 ± 5.7	3MF4R−H	503.9 ± 5.7
2MF5R−H	503.7 ± 5.7	3MF5R−H	502.4 ± 5.8
F2R−H	504.6 ± 5.6	F3R−H	505.0 ± 5.5

basis sets methods of Petersson et al., CBS-QB3 and CBS-APNO,[29,30] as well as Pople's G3[31] have been used with the application Gaussian-03.[32] In order to improve the precision of the results, an isodesmic set of reactions has been used in conjunction with reasonably well known enthalpies of formation for a small set of reference compounds.

We have assumed that the error associated with the computed enthalpy of reaction, which is one of the key sources of the final error of the target, is given by twice the appropriate standard deviation averaged over all three methods. The rationale for this approach, which errs very much on the side of caution, was introduced recently by Simmie et al.[33] and can be summarized as follows: The model chemistries CBS-QB3 and CBS-APNO provide independent determinations of the true ΔH_r value for each reaction and hence the average of these gives an obvious estimate of the true value. Although no error estimates are available for the individual ΔH_r values, we can use the differences to obtain an error estimate for the average value. Under the assumption that the CBS-QB3 and CBS-APNO values are independent determinations, X and Y, of the true value, the error in the differences is the same as that of the sum, $\sigma(X - Y) = \sigma(X + Y)$, and the error for the average is 1/2 of this. Examination of the differences suggests that the assumption of constant variability is reasonable (there is only very weak dependence of the differences on the average value) and hence the sample variance, σ_d^2, of the set of difference values can be used to estimate this variability. We can use $\sigma_d/2$ as the error estimate for the ΔH_r values in the subsequent overall error determination, but to allow for possible slight dependence in these determinations, we in fact use $2\sigma_d$—this provides us with a relatively conservative estimate of the overall error.

The above argument is possibly even stronger when three model chemistries are used, as here, as opposed to just two in our previous work. Note that it is essential to use more than one model chemistry to determine the uncertainty associated with reaction enthalpies and hence to determine the uncertainty associated with the target species. In addition uncertainties associated with a particular methodology determined from a test data set, for example, the popular G2 set,[34] are not readily transferable to a different collection of molecular species.

The methods employed give a good account of the known geometry of furan;[35] for example, the measured ∠COC of 106.5° is computed as 106.8°, 106.5°, and 106.6°, by CBS-QB3, CBS-APNO, and G3, respectively; ∠OCC of 110.65° as 110.5°, 111.0°, and 110.5°, while the bond distances are all within 1.5 pm. This agreement is most encouraging given that each method uses a different geometry optimization routine, viz., CBS-QB3 [B3LYP/CBSB7 ∼ 6-211G(2d,d,p)], CBS-APNO [QCISD/6-211G(d,p)], and G3 [MP2(Full)/6-21G(d)].

Molecules. Since data for furan itself[13] (F), and the alkylated 2,5-dimethyl- (25DMF), 2-*tert*-butyl- (TBF), and 2,5-di-*tert*-butylfurans (DTBF)[11] are to be used, the first question to be asked is are these internally consistent? By postulating the reaction

$$\text{F} + \text{DTBF} \rightarrow 2\text{TBF} \tag{1}$$

the calculated reaction enthalpy is given by

$$\Delta H_r/\text{kJ mol}^{-1} = 2(-163.8 \pm 0.76) + (293.9 \pm 1.4) + (34.7 \pm 0.7) = 1.0 \pm 1.9$$

using the data of Verevkin and Welle[11] and that of Guthrie et al.[13] whereas computations at CBS-QB3 and G3 yield ΔH_r = 1.19 and 0.81 kJ mol^{-1}, respectively. Unfortunately the requirements for a CBS-APNO calculation for 2,5-di-*tert*-butylfuran exceeded our computational resources and hence we cannot average over all three methods, but it is clear from this limited result that the data are internally consistent.

Once this has been established, we can proceed to compute the formation enthalpies of 2-methylfuran (2MF) via a set

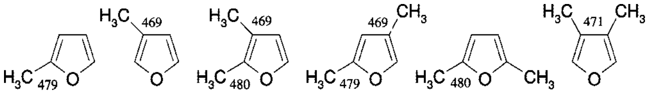

Figure 3. Ring-carbon−methyl bond dissociation energies/kJ mol^{-1}.

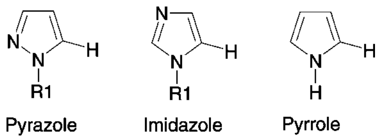

Figure 4. Pyrazoles, imidazoles, and pyrrole, C5−H highlighted.

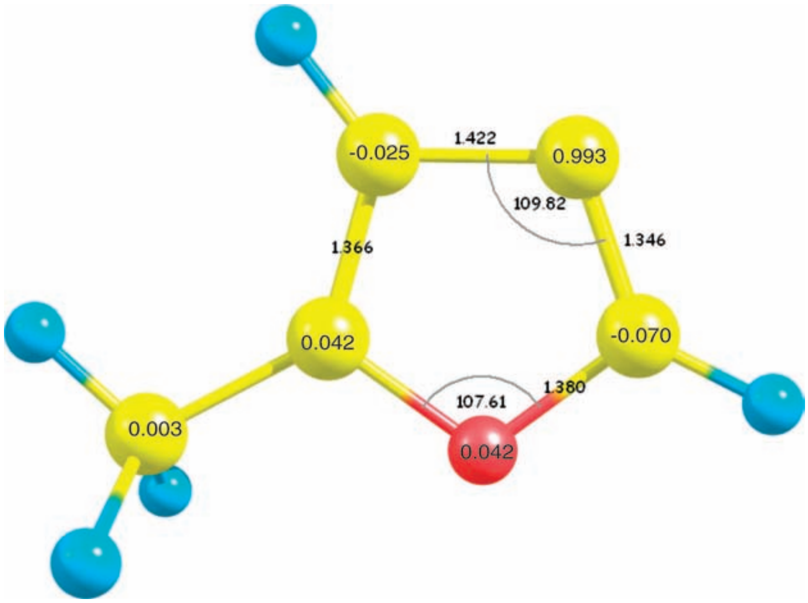

Figure 5. 2MF4R: geometry (Å and degrees) and spin densities at B3LYP/CBSB7.

TABLE 9: Internal Ring Angle Changes from Molecule to Radical (at B3LYP/CBSB7)

	change in ring angle/deg				
furan radical	1−2−3	2−3−4	3−4−5	4−5−1	5−1−2
F2R	**3.6**	−2.7	1.1	−0.8	−1.2
F3R	−2.6	**3.7**	−2.3	1.0	0.3
2MF2R	−1.6	0.4	0.5	0.8	−0.0
2MF3R	−2.5	**3.7**	−2.4	1.1	0.1
2MF4R	1.1	−2.4	**3.7**	−2.6	0.1
23DMF2R	−1.7	0.3	0.6	0.6	0.1
23DMF3R	−0.2	−2.0	0.3	0.8	0.0
25DMF3R	−2.6	**3.8**	−2.3	0.9	0.3

of isodesmic reactions which are listed in Table 1. Note in particular the high level of agreement between the three composite methods. A weighted average results in a final ΔH_f for 2-methylfuran of −80.8 ± 0.5 kJ mol^{-1}.

A direct comparison 2MF → 3MF yields reaction endothermicities of 11.25, 11.33, and 11.27 from CBS-QB3, CBS-APNO, and G3 multilevel methods, respectively; this implies $\Delta H_f = -69.5 \pm 0.5$ kJ mol^{-1} for 3-methylfuran (3MF).

The 2-position thus yields the more stable isomer as is the case for the monofluoro- and monochlorofurans[36] but not for furancarboxylic acids[37] which in view of the additional resonance possible between the furan O-atom and the COOH group is not surprising.

Previous estimates by Benson[38] for both 2-methyl- and 2,5-dimethylfuran of −69.2 and −104.8 kJ mol^{-1} are not in good agreement either with our computed value or with the measured value.[11]

The remaining disubstituted species 2,3-, 2,4-, and 3,4-dimethylfurans were computed by reference to 2,5-dimethylfuran; in terms of increasing stability the (2,5) is more stable than the (2,4) which in turn is more stable than the (2,3), and finally the (3,4) is the least stable—this exactly parallels the findings of Novak[36] for disubstituted fluorofurans.

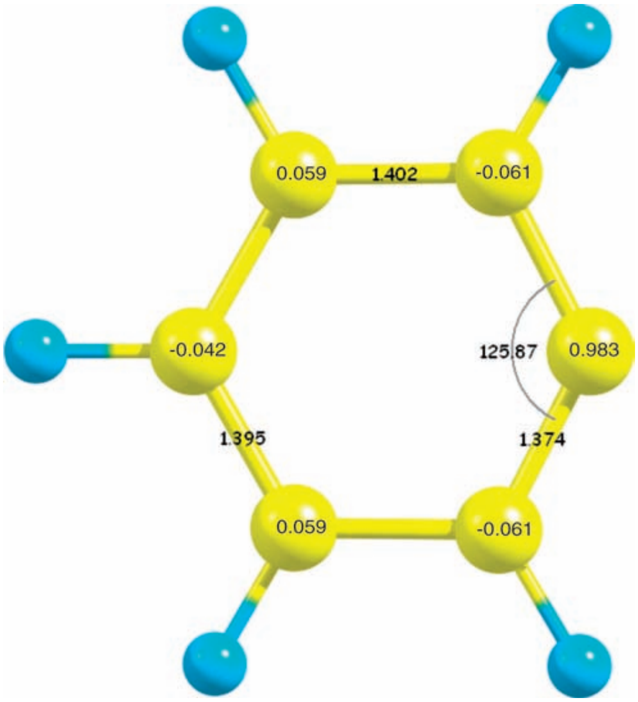

Figure 6. Phenyl radical: geometry and spin densities at B3LYP/CBSB7.

In a similar vein 2-vinylfuran (VF) can be determined from

$$\mathrm{VF + CH_2{=}CH_2 \rightarrow F + CH_2{=}CHCH{=}CH_2}$$

$$\mathrm{VF + C_6H_6 \rightarrow F + C_6H_5CH{=}CH_2}$$

$$\mathrm{VF + CH_3CH_3 \rightarrow 2MF + CH_3CH{=}CH_2}$$

as 13.7 ± 0.6 kJ mol^{-1}. This is not in agreement with a previous determination cited[39] by Pedley et al. of 27.8 ± 3.6 kJ mol^{-1} based on much earlier work by Landrieu et al.[12]

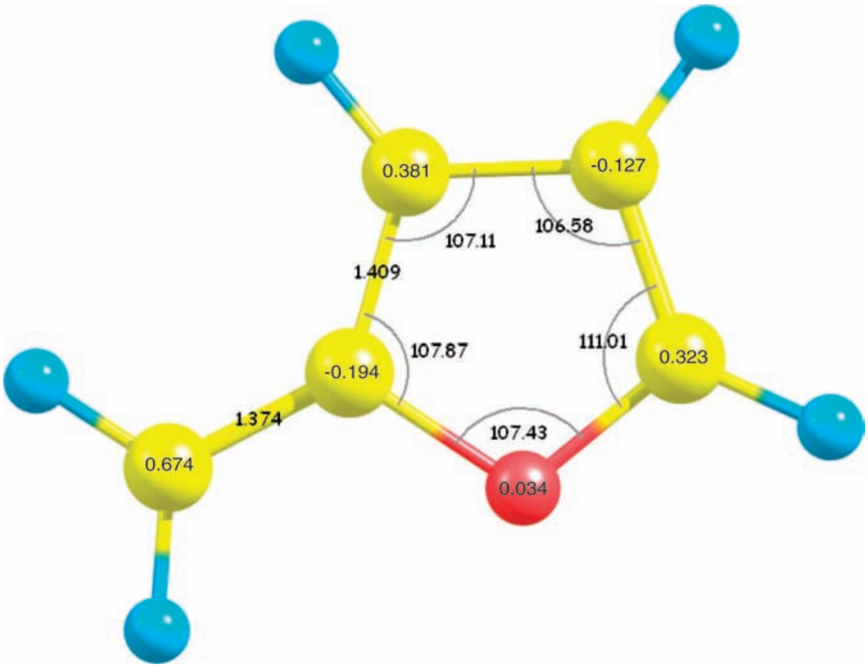

Figure 7. 2MF2R: geometry and spin densities at B3LYP/CBSB7.

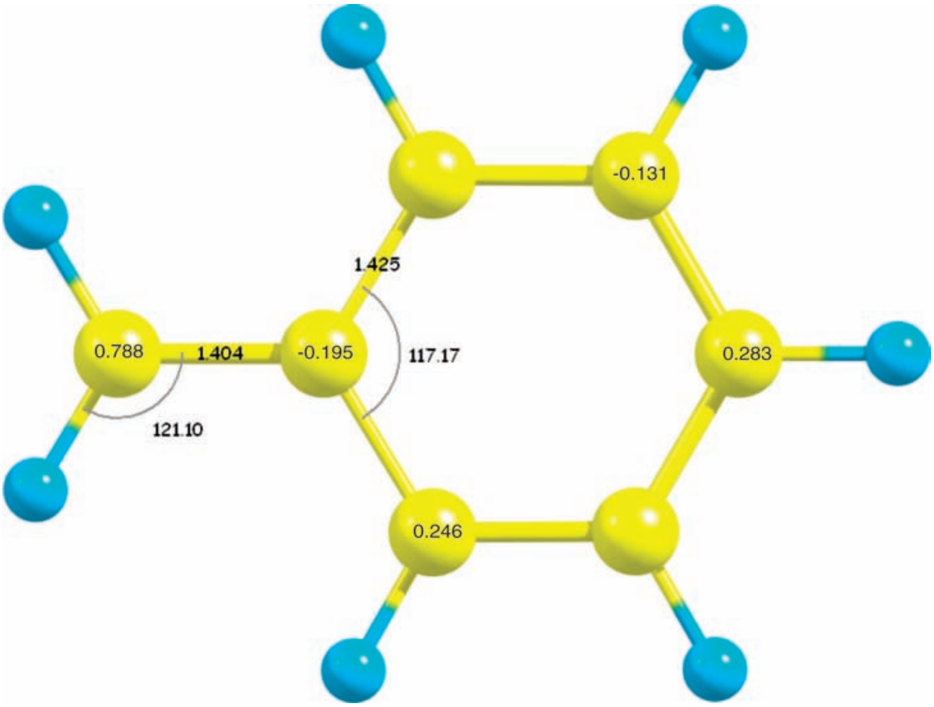

Figure 8. Benzyl radical: geometry and spin densities at B3LYP/CBSB7.

Finally, 2-ethylfuran can be computed from the established value for 2-methylfuran by way of a toluene/ethylbenzene and ethane/propane set of reference compounds. Table 2 contains all the enthalpies of formation determined in *this study*, and Table 3 contains the assumed values for the reference species.

There is another experimental measurement for the formation enthalpy of furan by Zaheeruddin and Lodhi[14] of −27.7 kJ mol^{-1} which is some 7 kJ mol^{-1} more positive than the value employed here due to Guthrie et al.[13] Adoption of −27.7 kJ mol^{-1} negates the consistency check outlined above, reaction 1, and considerably worsens the agreement obtained for 2-methylfuran from the set of isodesmic reactions. For these reasons we believe that the Guthrie et al.[13] number is closer to the true value. In their 2006 paper on an accurate and efficient method for predicting the thermochemistry of benzofurans and *o*-arynes Yu et al.[40] anchor their homodesmic calculations on the Guthrie et al. result.

Radicals. For the computation of the formation enthalpies of a series of radicals derived from dimethyl- and methylfurans, exactly the same approach was used. The reference radicals initially chosen were phenyl and benzyl which are probably the most suitable chaperons given that furans are regarded as “aromatics” albeit to a lesser extent than the prototypical benzene;[41] thus to determine the 5-methyl-2-furanmethyl radical, 25DMF2R, for example (see Figure 2 for nomenclature and structures of furyl, 2-methyl, and

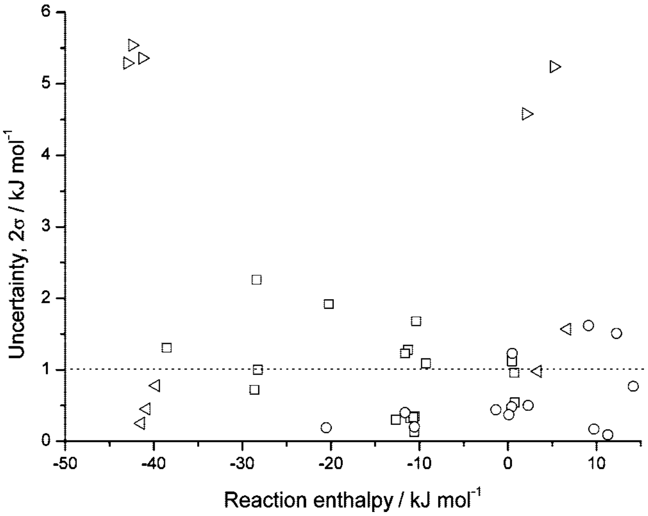

Figure 9. Uncertainty vs reaction enthalpy. Nature of reaction: triangle pointing right, radical + molecule; triangle pointing left, radical + molecule excluding G3 value; open box, radical−radical; open circle, molecule−molecule. The dotted line is intended solely as a visual aid.

2,5-dimethyl radicals; the 2,3-, 2,4-, and 3,4- compounds are named in a similar fashion) the reaction

$$\mathrm{25DMF2R} + C_6H_5CH_3 \rightarrow \mathrm{25DMF} + C_6H_5\dot{C}H_2 \quad (2)$$

was used, and for 2MF5R

$$\mathrm{2MF5R} + C_6H_6 \rightarrow \mathrm{2MF} + \dot{C}_6H_5 \quad (3)$$

However the results are poor; reaction endothermicities of 21.4, 21.7, and 17.2 are obtained for (2) and exothermicities of −19.5, −20.1, and −27.7 kJ mol^{-1} are obtained for (3).

The first result shows an uncertainty (2σ) of some 5 kJ mol^{-1} while the second amounts to 9 kJ mol^{-1}. Isodesmic reactions involving the phenyl radical thus show a greater scatter than those featuring benzyl, and the composite method G3 appears to deviate most from the mean. These discrepancies, which will impact on the accuracy with which the target species can be computed, are probably due to severe spin-contamination effects, Table 4. Hence alternative reference species were sought. In addition there is still, rather surprisingly, a major uncertainty surrounding the enthalpy of formation of the phenyl radical with recent values ranging from 329 to 340 kJ mol^{-1}.[42−47]

CBS-QB3 does include a spin correction term which is designed to minimize the error in highly spin-contaminated species although sometimes it overcompensates when dealing with less severely contaminated species. Variants have been put forward which provide some relief such as the restricted-open-shell ROCBS-QB3 procedure[48] or the CBS-RAD method.[49]

Although some improvement is seen for ROCBS-QB3 over standard CBS-QB3 in computed bond dissociation energies for benzene and toluene—which of course depend upon a successful calculation for phenyl and benzyl radicals—it does not appear in general to be a significant enough advance for radicals such as vinyl, $CH_2{=}\dot{C}H$, or allyl, $CH_2{=}CH\dot{C}H_2$, to warrant its adoption.[48]

The G3 multilevel procedure has also been reincarnated as G3-RAD and G3X-RAD to deal with open-shell species;[50] a summary of and a comprehensive explanation of a variety of composite methods can be found in Henry et al.[51] albeit that the results focus on very small systems containing, at most, three heavy atoms. A more recent account assesses a range of contemporary theoretical procedures for computing bond dissociation and radical stabilization energies and concludes that (in comparison to the multilevel method W1)[52] ROCBS-QB3, CBS-RAD, and CBS-QB3 "represent reliable and efficient procedures for calculating the thermochemistry of carbon-centered radicals".[53] Hence it was decided here to choose unsaturated, but not aromatic, radicals to replace the unsatisfactory combinations and keep the three multilevel methods.

Furyl. Three key radicals were chosen to base our results on: in the case of the dimethylfuryls, 25DMF3R, for the monomethyl furyls, 2MF3R, and F3R for the furyl radicals in conjunction with an ethene ($\Delta H_f = 52.57 \pm 0.21$) and vinyl ($\Delta H_f = 296.6 \pm 0.92$) combination.[54] Thus

$$\mathrm{25DMF3R} + CH_2CH_2 \rightarrow \mathrm{25DMF} + \dot{C}HCH_2 \quad (4)$$

$$\mathrm{2MF3R} + CH_2CH_2 \rightarrow \mathrm{2MF} + \dot{C}HCH_2 \quad (5)$$

$$\mathrm{F3R} + CH_2CH_2 \rightarrow \mathrm{F} + \dot{C}HCH_2 \quad (6)$$

The results exhibit very good agreement for the CBS methods with the G3 reaction enthalpy always more negative; for example for reaction 4 the enthalpies are −39.48 (CBS-QB3), −40.04 (CBS-APNO), and −44.37 (G3) which average to −41.30 ± 5.36 and in consequence ΔH_f(25DMF3R) = 157.2 ± 5.5 kJ mol^{-1}. If the G3 result is excluded, then the average exothermicity corresponds to −39.76 ± 0.78 kJ mol^{-1}. The net effect of this exclusion can be seen in the uncertainty which is markedly reduced in comparison to a much smaller change in the final enthalpy of formation of 25DMF3R from 157.2 ± 5.5 to 155.7 ± 1.6 kJ mol $^{-1}$. Much the same applies to reaction 5 for which reaction enthalpies of −40.67, −40.99, and −45.62 lead to −42.43 ± 5.54 and for (6) −41.54, −41.37, and −46.04 leads to −42.98 ± 5.29. Omitting the G3 data gives −40.83 ± 0.45 and −41.46 ± 0.25, respectively.

In G3MP2B3 calculations Sebbar and co-workers[61] determined values of 252.5 ± 5.3 and 255.1 ± 5.3 kJ mol^{-1} for 2-furyl and 3-furyl radicals; these are in good agreement with our values of 251.7 ± 5.5 and 252.1 ± 5.4 kJ mol^{-1}, respectively.

Once these key furyl radicals are established, the rest follow in a straightforward fashion; for 24DMF3R → 25DMF3R, ΔH_r = −10.42, −10.43, −10.73 and hence $\overline{\Delta H_r} = -10.52 \pm 0.35$ kJ mol^{-1}; for 2MF4R → 2MF3R we have ΔH_r = 0.53, 0.72, 1.06 with $\overline{\Delta H_r} = 0.77 \pm 0.54$ and finally for F2R → F3R ΔH_r = 0.81, 0.74, −0.19 $\overline{\Delta H_r} = 0.46 \pm 1.12$ kJ mol^{-1}.

The worst case scenario arises for 34DMF2R for which twice the standard deviation amounts to only ±1.9 in a reaction enthalpy of −20.2 kJ mol^{-1}; neglecting the G3 result changes the average to −19.7 ± 0.5. Hence omitting G3 data for these direct radical/radical reactions is hardly justified; conversely it can be argued that the G3 method could be dropped without significant error. However it is still of some use for those situations where a CBS-APNO calculation is computationally unfeasible. Wheeler et al.[62] have criticized the G3 method as suffering from large spin contamination in electronic wave functions, poor reference geometries, and anomalous vibrational frequencies but concluded that for isomerization reactions in the butadienyl system these sizable errors are largely canceled out, at least to within 4 kJ mol^{-1} of the results from more accurate methods.

The picture that emerges is reasonably coherent; for the monomethyl furans the 2 position yields the more stable radicals vis-à-vis the 3-position simply because 2-methylfuran is more stable than 3-methylfuran. The three different 2-methyl and 3-methyl radicals are of equal stability, that is, 2MF3R ≈ 2MF4R ≈ 2MF5R and 3MF2R ≈ 3MF4R ≈ 3MF5R.

Furfuryl. For the furfuryl radicals, two key radicals (24DMF2R or 4-methyl-2-furanylmethyl and 2MF2R or 2-furanylmethyl) were chosen and paired with propene[54] ($\Delta H_f = 20.24 \pm 0.41$) and allyl ($\Delta H_f = 165.2 \pm 2.3$) references

$$\text{24DMF2R} + \text{CH}_3\text{CHCH}_2 \rightarrow \text{25DMF} + \dot{\text{C}}\text{H}_2\text{CHCH}_2 \qquad (7)$$

$$\text{2MF2R} + \text{CH}_3\text{CHCH}_2 \rightarrow \text{2MF} + \dot{\text{C}}\text{H}_2\text{CHCH}_2 \qquad (8)$$

As before the G3 result is the outlier; for reaction 7 the heats of reaction are 7.23 (CBS-QB3), 6.11 (CBS-APNO), and 2.24 (G3) with a mean of 5.19 ± 5.24; omission of G3 gives 6.67 ± 1.57 kJ mol^{-1}. Similarly for reaction 8 the enthalpies are 3.70, 3.01, and −0.56 averaging to 2.05 ± 2.58 whereas omitting G3 gives 3.36 ± 0.98 kJ mol^{-1}.

Radical to radical conversions show much less scatter: for 24DMF4R → 25DMF2R the reaction enthalpies of −29.12, −28.92, −27.07 average to −28.37 ± 2.26 and become −29.0 ± 0.3 on neglecting the G3 datum. For 3MF3R → 2MF2R, −28.59, −28.45, and −27.66 ⟹ −28.23 ± 1.00 which similarly becomes −28.52 ± 0.19 kJ mol^{-1}. The cancelation of error, which is a feature of the isodesmic approach, is clearly evident here.

Note that the formation enthalpy for allyl is somewhat uncertain with Ellison et al. reporting a value of 173.2 ± 1.7 from flow tube experiments,[63] Tsang's value[64] of 171 ± 3 is widely quoted in compendia[65,6] whereas Seetula[66] measured a value of 166.1 ± 4.3 from the kinetics of allyl bromide photolysis and refers to previous results[67−69] of 165.2 ± 3.3, 164.8 ± 6.3, and 163.6 ± 6.3 in support of his own determination. The Third Millennium Thermodynamic Database[54] recommends 163.6 kJ mol^{-1}. Here we have adopted an average value of 165.2 ± 2.3 kJ mol^{-1}, not inconsistent with our previous work on alkyl hydroperoxides.[33] Adopting the higher Tsang value would raise the formation enthalpy of each *x*MF*x*R radical by 5.8 kJ mol^{-1} and consequently the bond dissociation energy $D(\text{C}-\text{CH}_3)$ by the self-same amount.

The new choices for reference species do improve the situation somewhat—partially because the effects of spin contamination are now more liable to be canceled out,[70] Table 4; compare phenyl/vinyl with the furyl radical 2MF4R and benzyl/allyl with the furfuryl radical 3MF3R.

A similar strategy was employed to determine enthalpies of formation for the four radicals derived from 3-methylfuran, the four each from the 2,3- and 2,4-dimethylfurans, and finally the two distinct radicals resulting from 3,4-dimethylfuran. The complete set of results for the radicals is given in Table 5.

Bond Dissociation Energies. Stein[71] estimated the C−H bond dissociation energy in the methyl group of 2-methylfuran at 361.9 ± 8.4 kJ mol^{-1} from very low pressure pyrolysis experiments.[72] This is in excellent agreement with our value of 360.9 ± 5.2 for 2-methylfuran and is typical of the corresponding bond for all the compounds studied, Table 6.

Note that for toluene values of $D(\text{C}_6\text{H}_5\text{CH}_2-\text{H})$ range from 369 through 381 with 375.5 ± 5.0 kJ mol^{-1} recommended.[6] The resonance stabilization energy, crudely defined as

$$\text{RSE}(\text{X}\dot{\text{C}}\text{H}_2) = D(\text{HCH}_2-\text{H}) - D(\text{XCH}_2-\text{H})$$

amounts to 78.4 kJ mol^{-1} for the 2-furfuryl radical (2MF2R) which is some 16 kJ mol^{-1} *greater* than the equivalent quantity for the benzyl radical.[6] Therefore hydrogen atom abstraction from the methyl group should occur more readily in furans than in methyl-substituted benzenes.

The ring-carbon methyl bond strengths, $D(\text{R}-\text{CH}_3)$, in methyl- and dimethylfurans are roughly the same at approximately 480 and 470 kJ mol^{-1} for the 2- and 3-positions, respectively, Table 7 and Figure 3; much stronger than the comparable bonds in toluene (427 kJ mol^{-1}) or propene (426 kJ mol^{-1}) and indeed almost as strong as the central bond in 1,3-butadiene (489 kJ mol^{-1}).[6] Although Lifshitz et al.[10] took into account the strengthening effect of the $\alpha-\beta$ double bond in their estimation of the C−CH$_3$ bond energy in 2,5-dimethylfuran, their result of 410 kJ mol^{-1} differs substantially from our computed one.

For 2-ethylfuran the R−CH$_3$ bond strength declines sharply to 310 ± 5 kJ mol^{-1} in agreement with the 313.8 ± 8.4 kJ mol^{-1} estimated by Stein,[71] and in line with the collapse[6] seen in going from toluene to ethylbenzene of 426.8 ± 4.2 kJ mol^{-1} → 325.1 ± 4.2 kJ mol^{-1}.

The ring C−H energies in both methyl- and dimethylfurans and furan itself are all essentially the same at approximately 504 kJ mol^{-1}, Table 8, considerably stronger than the estimate of 469 kJ mol^{-1} by Lifshitz et al.[10] Note that the corresponding bond in an aromatic such as benzene[6] is considerably weaker at 472 kJ mol^{-1}. So H-abstraction from ring hydrogens in furans is much less likely than that from typical aromatics.

The computed dissociation energies, for the ring-carbon hydrogen bonds (in excess of 500 kJ mol^{-1}) do at first sight appear somewhat extreme although they are still weaker than that in H−C≡N which at 528.5 ± 0.8 kJ mol^{-1} is probably the strongest C−H bond known.[73] Interestingly other five-membered heterocycles have very recently been shown to have comparable values. For example, the C5−H bond energies have been measured by negative ion spectroscopy and gas-phase ion chemistry for pyrazole[74] (R1 = H, 506 ± 17 kJ mol^{-1}), N-methylpyrazole[75] (R1 = methyl, 493 ± 3 kJ mol^{-1}), and N-methylimidazole[75] (R1 = H, 508 ± 4 kJ mol^{-1})—compounds not unrelated to the furans, Figure 4. In addition, an earlier shock tube study of the decomposition of pyrrole was suggestive of $D(\text{C}-\text{H})$ of 495.4 ± 4.2 kJ mol^{-1}.[76] da Silva and co-workers[77] have shown from theoretical calculations at G3, G3B3, and CBS-APNO levels that very strong C−H bonds, ranging from 493 to 523 kJ mol^{-1}, are to be found in pyrrole, pyrazole, imidazole, and tri- and tetrazoles.

The usual explanation advanced to account for such strong C−H bonds is that the radical formed is of a very low *thermodynamic* stability. Barckholtz et al.[78] in a perceptive study of small aromatic heterocycles including furan—representative of the functionalities in coal—showed that geometric and spin density factors can be used to understand the relative stability of the radicals formed. For five-membered rings the spin density tends to be localized at the radical site and thus there is no resultant stabilization of the newly formed radical via delocalization. They used a number of different ab initio and DFT methods to compute C−H and N−H bond energies but finally chose B3LYP/6-21G(d) on the basis of comparisons with the limited experimental data available to them at that time. They calculated D(C2−H) = D(C3−H) ≈ 495 kJ mol^{-1} for furan, some 32 kJ mol^{-1} stronger than the comparable bond in benzene; if their difference can be transferred to the currently accepted value for benzene,[6] then furan C−H energies of ca. 502 kJ mol^{-1} would have resulted, which is in agreement with the 505 ± 6 kJ mol^{-1} from *this study*.

The alkylfurans behave in a similar manner; the spin density is localized at the radical site, see Figure 5, and geometrical changes in the furyl radical structures, computed via B3LYP/CBSB7 which is the optimizer for CBS-QB3, are mainly confined to the $X-\dot{C}-C$ angle which opens out by 3.7° from the neutral molecule, Table 9, with the neighboring angles compensating. The C−O−C or 5−1−2 angle is largely unaffected in all cases. Comparison with the phenyl radical is instructive, Figure 6.

By way of contrast radical formation at the methyl group where $^{\bullet}CH_2$ is formed, for example, in the furfuryl radicals 2MF2R, 3MF3R, 23DMF3R, 25DMF2R, etc. causes the ring angle to *decrease* but by a smaller amount, ~1.7° for the particular case of the 2-furanylmethyl radical, Figure 7. The major change is the contraction of the carbon−carbon distance, $H_3C-C \Rightarrow H_2-\dot{C}-C$, by 0.10−0.12 Å, which is similar to the geometrical changes evident in the transition from toluene ⇒ benzyl of −0.11 Å and −1.0°. The Mulliken atomic spin density is slightly more dispersed for furfuryl vis-à-vis benzyl; cf. Figures 7 and 8. Hence the weaker C−H bonds.

The heat of formation of the furfuryl radical (2MF2R) was determined by Chowdhury et al.[79] as 106 ± 12 kJ mol^{-1} in a study of the photodissociation of furfuryl alcohol (2-hydroxymethylfuran, 2MFOH) by monitoring the production of hydroxyl radicals via laser-induced fluorescence. They estimated a bond dissociation energy of about 357 kJ mol^{-1} for the H_2C-OH bond based upon a threshold dissociation energy from RRKM calculations and the well-known BDE for methanol, H_3C-OH, of 376 kJ mol^{-1}. In turn this implies a radical stabilization energy of 19 kJ mol^{-1}. However we have already shown that the radical stabilization energy is substantially greater than this and hence we predict from our calculations

$$\begin{aligned} D(\mathrm{C-OH}) &= \Delta H_f(\mathrm{2MF2R}) + \Delta H_f(\dot{\mathrm{O}}\mathrm{H}) - \Delta H_f(\mathrm{2MFOH}) \\ &= (62.0 \pm 5.2) + (37.34 \pm 0.04) + (211.8 \pm 2.1) \\ &= 311.1 \pm 5.6 \ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

So the C−OH bond is much weaker at ≈311 kJ mol^{-1}; note that the comparable bond in benzyl alcohol[6] ranges from 334 to 340 kJ mol^{-1}.

Halofurans. Novak[36] used high-level G3 calculations and isodesmic reactions to provide accurate enthalpies of formation for a number of polyfluoro- and chlorofurans. His results can now be used in conjunction with our own for the 2- and 3-furfuryl radicals to compute C−F bond and C−Cl bond dissociation energies in these compounds. Adopting the atomic enthalpies of formation given by Luo[6] of $\Delta H_f(\dot{F}) = 79.38 \pm 0.30$ kJ mol^{-1} and $\Delta H_f(\dot{Cl}) = 121.301 \pm 0.008$ kJ mol^{-1} the bond dissociation energy is 549 kJ mol^{-1} for 2-fluorofuran and 535 kJ mol^{-1} for 3-fluorofuran; both of these are stronger than the reported 525.5 ± 8.4 kJ mol^{-1} for monofluorobenzene[39] and the first exceeds the strongest currently known C−F of 547 kJ mol^{-1} in tetrafluoromethane and tetrafluoroethene.[6] Note that the difference between the two isomers stems wholly from the differences in Novak's computed molecular formation enthalpies.

In the case of the chloro compounds the two bond strengths are practically the same at 427 for 2-chloro and 424 for the 3-chloro furan − again substantially stronger than the 400 in the corresponding chlorobenzene[6] and nearly as strong as the strongest known C−Cl bond encountered in dichloroacetylene, Cl−C≡CCl, by Lias et al.[80] of 443 ± 50 or that computed by Zhu and Bozzelli[81] of 464 ± 46 kJ mol^{-1}.

Conclusions

In summary it can be seen that for stable closed shell molecules the three multilevel methods are in excellent agreement with each other and yield precise reaction enthalpies whose standard deviation is less than 1 kJ mol^{-1}; see circles in Figure 9. The uncertainties in the enthalpy of formation of the target species are therefore largely determined by the uncertainties of the reference compounds. By considering a number of working reactions, this uncertainty can, in favorable circumstances, be markedly reduced and is less dependent upon the individual references.

In the case of open-shell species the paucity of reliable reference radicals necessitated a change of approach which now relies totally on a single compound. This does have the advantage that future refinements in the values of $\Delta H_f(CH_2{=}CH\dot{C}H_2)$ or $\Delta H_f(CH_2{=}\dot{C}H)$ allow an easy recalculation of the results obtained here.

Once key furyl and furfuryl radicals have been determined, the computation of other members of these families is facilitated by the generally excellent results for reaction enthalpies of radical → radical comparisons. Note that the maximum standard deviation is less than 1 kJ mol^{-1} for virtually all of these reactions; see squares in Figure 9.

The agreement is particularly good when one compares 2-furyl radicals with each other or 3-furyl radicals also with each other; the scatter increases in 2- versus 3-comparisons but not to any significant extent. Fundamentally G3 cannot do as good a job in measuring the $\dot{C}-O$ interaction vis-à-vis the lesser $\dot{C}-CH-O$ interaction. The same conclusion applies to molecule + radical working reactions where the uncertainty is approximately 5 kJ mol^{-1} but falls to less than 2 kJ mol^{-1} when the G3 value is excluded; see triangles in Figure 9.

The published experimental enthalpies of formation for furan,[13] 2,5-dimethyl-, 2-*tert*-butyl-, and 2,5-di-*tert*-butylfurans appear to be self-consistent, that for 2-vinylfuran does not. We have determined ΔH_f(298.15 K) for 2-ethyl, both 2- and 3-methyl, the disubstituted 2,3-, 2,4-, and 3,4-isomers, and nearly every single radical derived from the preceding molecules.

The bond dissociation energies which can then be computed from the above results are in very good agreement with the very limited existing data, namely, that for the RCH_2-H in 2-methylfuran and the side-chain carbon−carbon bond, $D(R-CH_3)$, in 2-ethylfuran.[71] Our findings can be summarized as follows:

- Extremely strong ring-carbon to hydrogen (also carbon−fluorine and carbon−chlorine) bonds arising out of the thermodynamic instability of the resulting furyl radicals not able to delocalize the spin density at the radical site and the relative inflexibility of the five-membered furan ring to accommodate geometrical distortion as the radical forms.
- Very strong ring-carbon to methyl bonds for much the same reasons as the above.
- Relatively weak side-chain carbon to hydrogen bonds (and carbon to OH) in comparison to methyl-substituted benzenes.

Consequently the enhanced reactivity on going from furan to polyalkylated furans, as regards H-atom abstraction, is readily understood.

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Supporting Information Available: A complete listing of each working reaction, computed enthalpies at 298.15 K, and formation enthalpies employed. This material is available free of charge via the Internet at http://pubs.acs.org.

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