

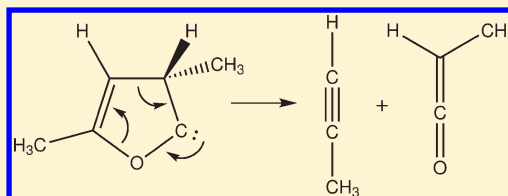
# Ab Initio Study of the Decomposition of 2,5-Dimethylfuran

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Supporting Information

**ABSTRACT:** The initial steps in the thermal decomposition of 2,5-dimethylfuran are identified as scission of the C–H bond in the methyl side chain and formation of  $\beta$ - and  $\alpha$ -carbenes via 3,2-H and 2,3-methyl shifts, respectively. A variety of channels are explored which prise the aromatic ring open and lead to a number of intermediates whose basic properties are essentially unknown. Once the furan ring is opened demethylation to yield highly unsaturated species such as allenylketenes appears to be a feature of this chemistry. The energetics of H abstraction by the hydroxyl radical (and other abstracting species) from a number of mono- and disubstituted methyl furans has been studied. H-atom addition to 2,5-dimethylfuran followed by methyl elimination is shown to be the most important route to formation of the less reactive 2-methylfuran. Identification of 2-ethynylfuran as a  $C_6H_6O$  intermediate in 2,5-dimethylfuran flames is probably not correct and is more likely the isomeric 2,5-dimethylene-2,5-dihydrofuran for which credible formation channels exist.



## INTRODUCTION

Synthesis of new biofuels by second-generation methods of production from biomass is one of the most exciting developments of recent times, transforming abundant renewable resources, but not crops destined for human or animal consumption, into liquid transport fuels.<sup>1–3</sup> In particular, biofuels which possess significant advantages over the current market leader, ethanol, regarding performance in an internal combustion engine<sup>4</sup> and physical properties are actively being sought.<sup>5,6</sup> Chief among these is 2,5-dimethylfuran (25DMF), whose blending research octane number makes it nearly twice as effective on a molar basis as ethanol<sup>7–9</sup> and whose energy density is close to that of gasoline. The laminar burning velocity of 25DMF closely matches that of gasoline and differs from that of ethanol by some 30%.<sup>10</sup>

The chemical synthesis of 25DMF from authentic, inedible, lignocellulosic material, untreated maize leaves and stalks, is particularly noteworthy,<sup>11</sup> but other routes are also promising.<sup>12</sup> However, the combustion chemistry of 25DMF is almost totally unknown; exploration of this chemistry is the aim of this work. The first studies of the combustion and emissions of 2,5-dimethylfuran in a direct-injection spark-ignition engine have just been published.<sup>13,14</sup>

The thermal unimolecular decomposition of 2,5-dimethylfuran was studied at low pressures between 1050 and 1270 K by Grela et al.,<sup>15</sup> who speculated that rearrangement to 2,4-dimethylfuran occurs, via a cyclopropenylcarbonyl intermediate, prior to elimination of carbon monoxide.

Lifshitz et al.<sup>16</sup> studied the thermal decomposition of 2,5-dimethylfuran behind reflected shock waves, over a not dissimilar temperature range, sampling and quantitatively analyzing the degradation products. They assembled a reaction scheme comprising 50 species and some 180 elementary reactions with the majority of the kinetic and thermochemical parameters being

estimated. In agreement with Grela et al.<sup>15</sup> they found that the rate of decomposition increases with increasing methylation from furan through 2-methylfuran to 2,5-dimethylfuran.

Their decomposition channels included scissions of the C–CH<sub>3</sub> and CH<sub>2</sub>–H bonds based on bond dissociation energies (BDEs) of 410 and 368 kJ mol<sup>–1</sup>; they discounted cleavage of the ring-carbon–H bond because of a bond dissociation energy of 469 kJ mol<sup>–1</sup>. However, their estimated BDEs are substantially in error; updated values are shown in Figure 1, where the quoted values (in kJ mol<sup>–1</sup>) have been taken from a more recent publication by Simmie and Curran.<sup>17</sup>

The very strong ring-carbon to hydrogen bonds predicted in that work<sup>17</sup> of >500 kJ mol<sup>–1</sup> for furan itself and for mono- and dimethylfurans has since received confirmation. Vogelhuber et al.,<sup>18</sup> in a first ever experimental determination, used photoelectron spectroscopy of the cyclic furanide anion to measure the electron affinity of the furanyl radical and, in combination with the known gas-phase acidity of furan, determined a BDE (C–H<sub>α</sub>) of 501.2 ± 8.4 kJ mol<sup>–1</sup>.

Lifshitz et al. considered that carbon monoxide elimination was routed through a 1,2-methyl transfer to form a carbene, which then led to a number of C<sub>5</sub>H<sub>8</sub> species including 1,2-, 1,3-, and 2,3-pentadienes and 2-pentyne.

Since the furfuryl radical, 5-methyl-2-furanylmethyl (25DMF2R), is undoubtedly the most likely radical to be formed from the parent compound its reactions are very important. Complex scissions of the radical to yield acetyl radicals were considered, as were CO elimination steps.

The Mackie group<sup>19</sup> carried out ab initio CASPT2 and G2- (MP2) quantum chemical studies of the pyrolysis of furan and

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computed four unimolecular decomposition pathways including a 2,3 (and 3,2) H-transfer reaction leading to carbene formation, Figure 2, with barriers of ca.  $275 \text{ kJ mol}^{-1}$ . The carbene can then fragment eventually to yield ketene,  $\text{H}_2\text{C}=\text{C}=\text{O}$ , and acetylene,  $\text{HC}\equiv\text{CH}$ .

Previously, Liu and co-workers<sup>20</sup> carried out a theoretical investigation of the unimolecular decomposition channels of furan at levels up to QCISD(T)/6-311++G\*\* on geometries optimized at B3LYP/6-31G\*\*. In addition to the intermediate carbene shown above, they considered the fate of the  $\beta$ -carbene which ultimately results in formation of propyne (methylacetylene),  $\text{HC}\equiv\text{C}-\text{CH}_3$ , and carbon monoxide, Figure 3.

The most clear-cut evidence for thermal decomposition channels of furan come from the very recent work of Vasiliou et al.,<sup>21</sup> who have shown in elegant flow reactor experiments at 1600 K that acetylene, ketene, carbon monoxide, and propyne are all formed initially with the propargyl radical making an appearance at higher temperatures. They used the G2(MP2) calculations of Sendt et al.<sup>22</sup> to rationalize their results and concluded that pyrolysis of furan is routed through carbenes formed by 1,2- and 2,1-H-atom transfers.

Very recently, Wu et al.<sup>23</sup> studied the intermediates formed during oxidation of 2,5-dimethylfuran in a low-pressure premixed laminar flame by tunable vacuum-ultraviolet photoionization and molecular beam mass spectrometry. This sophisticated technique, which employs synchrotron radiation, can provide isomer specific qualitative (and in some cases quantitative) analysis of both stable and transient species. In the case of fuel-rich 2SDMF flames, Wu et al. detected a large number of compounds ranging from methyl radical to 2-methylnaphthalene. Some of the intermediates were identified by comparing computed ionization energies, probably from G3 calculations but with a 6-311++G(2d,p) basis set, with those measured experimentally. In addition, they also report bond dissociation energies, computed

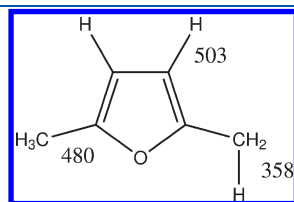


Figure 1. Bond dissociation energies.

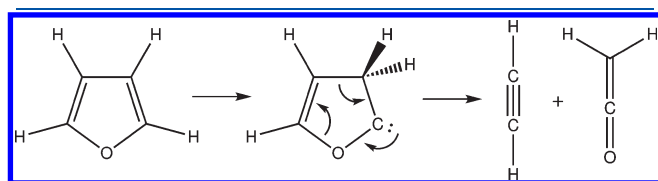


Figure 2. Formation and fate of  $\alpha$ -carbene.

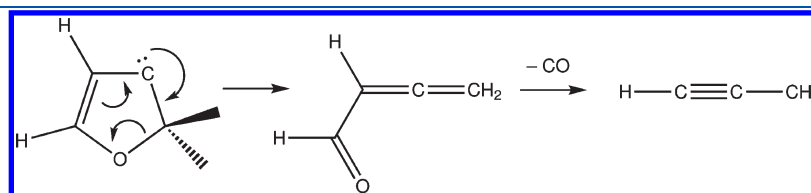


Figure 3. Fate of  $\beta$ -carbene.

in an unspecified manner, of  $535 \text{ kJ mol}^{-1}$  for the ring–methyl group,  $531 \text{ kJ mol}^{-1}$  for ring–carbon–H bond, and  $370 \text{ kJ mol}^{-1}$  for the same bond in the methyl side chain. These values, particularly those involving the furan ring, are somewhat higher than those currently accepted.<sup>17</sup>

Zhang et al.<sup>24</sup> studied the mechanism of the reaction between  $\dot{\text{O}}\text{H}$  and 3-methylfuran at G3MP2 and G3MP2B3 levels of theory which are based on MP2(full) and B3LYP geometries with a 6-31G(d) basis, respectively. As regards the ring-H-abstraction endothermic channels they found that barriers of 45.2, 39.9, and  $48.9 \text{ kJ mol}^{-1}$  exist for the 2, 4, and 5 positions, while the barrier for the highly exothermic abstraction from the methyl group was only  $12.1 \text{ kJ mol}^{-1}$ . Thus, for ring-H abstraction, positions adjacent to the heterocyclic O atom have a slightly higher barrier than the position remote from O; this is in contrast to our recent finding<sup>17</sup> that the ring–carbon–H bond strengths are all the same, essentially regardless of the number or the location of methyl groups on the ring.

Their study<sup>25</sup> of the reactions between  $\dot{\text{O}}\text{H}$  and 2-methylfuran by contrast present quite a different picture; now they found that ring-H abstraction from the 3 and 5 positions have barriers in excess of  $110 \text{ kJ mol}^{-1}$  but that from the 4 position is only  $36 \text{ kJ mol}^{-1}$ . Abstraction from the methyl side chain on the other hand is very similar to that found for 3-methylfuran. In a later study of  $\dot{\text{O}}\text{H}$  + 2-ethylfuran<sup>26</sup> they report similar barriers to the 2-methylfuran case at G3MP2 and G3MP2B3 levels of theory for direct abstraction at positions 3 and 4 on the ring and from the side chain methyl group. They found that addition–elimination reactions are more important and report that both pre- and postreaction weakly bound complexes are formed.

Here, we are primarily interested in the energetics of the early stages in the thermal decomposition of 2,5-dimethylfuran, in particular those reactions which prise the ring open to yield acyclic hydrocarbon and/or oxygenated species whose combustion chemistry is at least somewhat better known than that of furan derivatives.<sup>27</sup> These efforts are directed at complementing our experimental<sup>28</sup> and our ongoing modeling<sup>29</sup> work on this next-generation biofuel.

In addition, the literature concerning hydrogen-atom abstraction from the furan ring and from substituent methyl groups by the hydroxyl radical, an important class of reactions at medium to high temperatures, seems somewhat contradictory, hence our attempt to resolve this perceived anomaly.

## CALCULATION METHODS

The compound methods CBS-QB3<sup>30</sup> and CBS-APNO,<sup>31</sup> G3,<sup>32</sup> and G3MP2B3<sup>33</sup> were employed to compute the geometries and energies of the reactants, transition states, and products via the applications G-03 and G-09,<sup>34</sup> with visualization, etc., provided by ChemCraft.<sup>35</sup> Unless otherwise stated, barriers and reaction energies refer to  $\Delta E^\ddagger(0 \text{ K})$ , which includes the zero-point energy. Intrinsic reaction coordinate calculations were

utilized to connect transition states with reactants and products. Adiabatic ionization energies, averaged over all three composite methods, are reported as  $\Delta E(0\text{ K})[M^+ - M] \pm 2\sigma$ .

Rate constant calculations, based on canonical transition state theory, were performed with the MultiWell-2010 program suite via the thermo application.<sup>36</sup> Frequency scaling factors, appropriate to the optimization method employed, were used and a proper account taken of hindered internal rotors by relaxed scans of both reactant(s) and transition states. Although scaling factors for a particular model chemistry are both temperature and property dependent,<sup>37</sup> this aspect has been neglected here. The ensuing rate constants are reported as two- or three-parameter Arrhenius-type equations.

In employing more than one model chemistry, which is a theoretical method and basis set, one can obtain some impression of the uncertainty associated with the barrier heights and reaction enthalpies. In a few cases rate constants were computed from the three principal composite methods used and the results compared in order to obtain an appreciation of the uncertainty of the kinetics. Thus, for hydrogen-atom abstraction from a methyl group in 25DMF by a H atom, the following rate constants could be calculated ( $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$ )

$$\text{CBS-QB3 } k = 1.22 \times 10^6 T^{2.407} \exp(-2148/T)$$

$$\text{CBS-APNO } k = 4.32 \times 10^5 T^{2.664} \exp(-2082/T)$$

$$\text{G3 } k = 3.86 \times 10^5 T^{2.679} \exp(-2683/T)$$

Thus, the uncertainty in  $k$  amounts to approximately 50% throughout the range 500–2000 K.

## RESULTS AND DISCUSSION

**Bond Scission.** Hydrogen-atom formation resulting from cleavage of the  $\text{CH}_2\text{—H}$  bond is the most likely process given the remarkable strength of ring-C— $\text{CH}_3$  and ring-C—H bonds. Indeed, Olzmann and co-workers<sup>38</sup> measured the rate of formation of H atoms by atomic resonance absorption spectrometry on shock heating 25DMF and reported a rate constant of  $3.47 \times 10^{16} \exp(-42\,820/T) \text{ s}^{-1}$  at temperatures of 1250–1550 K and at pressures of 1.6–4.7 bar. Their activation energy of  $356 \text{ kJ mol}^{-1}$  is in good agreement with the computed BDE of  $357.8 \pm 5.9 \text{ kJ mol}^{-1}$  by Simmie and Curran<sup>17</sup> and with the averaged value of  $356.0 \pm 8.9 \text{ kJ mol}^{-1}$  reported by Hayes and Hadad for the comparable bond in 2-methylfuran.<sup>39</sup>

However, a recent determination of the formation enthalpy of the allyl ion,  $\text{C}_3\text{H}_5^+$ , by threshold photoelectron–photoion coincidence spectroscopy by Shuman et al.<sup>40</sup> lead them to an evaluation for the allyl radical,  $\dot{\text{C}}\text{H}_2\text{CH=CH}_2$ , of  $\Delta H_f(298.15\text{ K}) = 170.9 \pm 2.5 \text{ kJ mol}^{-1}$ . This value lies closer to the two most positive values<sup>41,42</sup> of  $171 \pm 4$  and  $173.2 \pm 2.1$  and furthest from others<sup>43–45</sup> of  $163.6 \pm 6$ ,  $164.8 \pm 6$ , and  $167.4 \pm 4 \text{ kJ mol}^{-1}$ . Since the calculations of formation enthalpies for furfuryl radicals<sup>17</sup> were anchored on a compromise  $\Delta H_f(298.15\text{ K}) = 165.2 \pm 2.3 \text{ kJ mol}^{-1}$  for allyl, adoption of the new allyl value would increase the formation enthalpy of the furfuryl radicals by  $5.7 \text{ kJ mol}^{-1}$ . In turn, this increases the calculated BDE by the same amount; hence, the revised side chain BDE  $\text{CH}_2\text{—H}$  is now somewhat stronger at  $357.8 + 5.7 = 363.5 \pm 5.9 \text{ kJ mol}^{-1}$ .

Additional H atoms can be produced on shock heating 25DMF by scission of the C—H bond in the methyl group of

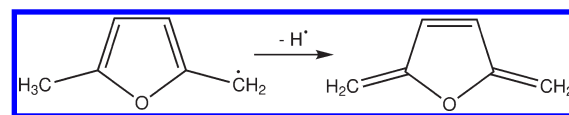


Figure 4. Formation of 2,5-dimethylene-2,5-dihydrofuran.

the 5-methyl-2-furanylmethyl radical (25DMF2R),  $k = 1.66 \times 10^{15} \exp(-29\,997/T) \text{ s}^{-1}$ , to give 2,5-dimethylene-2,5-dihydrofuran, Figure 4. This  $\text{C}_6\text{H}_6\text{O}$  compound is not well known but is produced in high yield by flash pyrolysis of 5-methyl-2-furanylmethyl benzoate at subatmospheric pressures and temperatures of around 915 K; mechanistically, it is thought that migration of benzoate across the furan ring leads to O addition at the methyl ring carbon followed by elimination of benzoic acid.<sup>46,47</sup>

Two  $\text{C}_6\text{H}_6\text{O}$  species were detected by Wu et al.,<sup>23</sup> which they identified as 2-ethenylfuran and phenol on the basis of their ionization energies. Thus, the observed IEs of  $7.95$  and  $8.51 \text{ eV}$  were ascribed to 2-ethenylfuran with a calculated IE of  $7.86 \pm 0.15 \text{ eV}$  and phenol with a literature value of  $8.508 \pm 0.001 \text{ eV}$ .<sup>48</sup> Although 2-ethenylfuran (2-vinylfuran) is a possible intermediate, note that we compute an IE of  $7.95 \pm 0.08 \text{ eV}$  for 2,5-dimethylene-2,5-dihydrofuran and values of  $8.12 \pm 0.03 \text{ eV}$  for either conformer (cis/trans O—C=C=C) of 2-ethenylfuran. Hence, it is probable that the dimethylene compound is formed in 2,5-dimethylfuran flames, but a more sophisticated method of analysis such as tandem mass spectrometry will be required for positive identification.

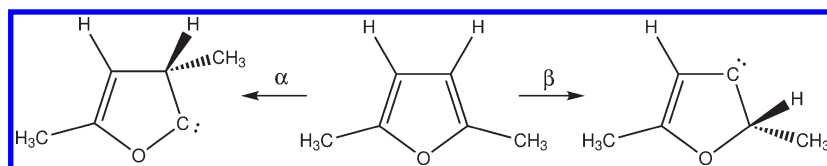
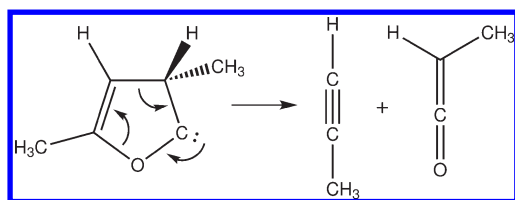
A not dissimilar sequence arises in the thermal decomposition of *p*-xylene (1,4-dimethylbenzene),<sup>49,50</sup> where the initial scission of  $\text{CH}_2\text{—H}$  is followed by scission of the same bond in the resulting *p*-methylbenzyl radical to presumably form *p*-xylylene; activation energies of  $380$  and  $294 \text{ kJ mol}^{-1}$  were indicated, although the latter figure has been questioned and a lower value of  $257 \text{ kJ mol}^{-1}$  proposed.<sup>51</sup> The evidence for *p*-xylylene formation is not definitive in flow reactor<sup>52</sup> and shock tube<sup>50</sup> experiments, although it is often presumed formed; kinetic rather than thermodynamic instability is at fault.<sup>53</sup>

H-atom production from scission of the ring-C—H bond in 2,5-dimethylfuran is disfavored by a factor of more than  $7 \times 10^3$  over the temperature range 500–2000 K; this result is obtained by comparing the calculated equilibrium constants and on the assumption that the recombination rate constants are identical. The increase in pyrolytic reactivity noted by Grela et al.<sup>15</sup> and Lifshitz et al.<sup>16,54</sup> in going from furan to 2-methylfuran to 2,5-dimethylfuran is thus obvious.

**Formation of Carbenes.** *Ring-H- and Methyl-Transfer Reactions.* The migrations of a ring H atom and that of a methyl group have been suggested as possibilities in order to explain the product distribution found in shock waves and in flames. Liu and co-workers<sup>20</sup> found that a 3,2-H shift in furan had a barrier of  $270 \text{ kJ mol}^{-1}$ , the resultant  $\beta$ -carbene then fragmenting to ketene + acetylene ( $117 \text{ kJ mol}^{-1}$ ) or to methylacetylene + CO ( $181 \text{ kJ mol}^{-1}$ ).

Comparable results were obtained by Sendt and co-workers at G2(MP2) with formation of the  $\alpha$ -carbene, following a 2, 3-H shift, needing to surmount a barrier of  $272 \text{ kJ mol}^{-1}$  and the  $\beta$ -carbene, formed by a 2,3-H shift, having to surmount  $289 \text{ kJ mol}^{-1}$ .

In the case of 2,5-dimethylfuran, only 3,2-H and 2,3- $\text{CH}_3$  transfers are possible, Figure 5. First, we consider H-atom transfer resulting in formation of a  $\beta$ -carbene. A singlet transition

Figure 5. Formation of  $\alpha$ - and  $\beta$ -carbenes.Figure 6. Decomposition of 25DMF  $\alpha$ -carbene.

state can be located at both CBS-QB3 ( $289.4 \text{ kJ mol}^{-1}$ ) and G3 ( $287.1 \text{ kJ mol}^{-1}$ ) above 25DMF; these values are very similar to the 3,2-H-transfers calculated for furan by Liu et al.<sup>20</sup> and Sendt et al.<sup>22</sup> of  $272\text{--}289 \text{ kJ mol}^{-1}$ ; however, the singlet  $\beta$ -carbene product does not exist at CBS-QB3 but optimizes instead to hexa-3,4-dien-2-one, a product of ring opening.

Second, the transfer of a methyl group which results in an  $\alpha$ -carbene has been computed; we calculate remarkably consistent barriers of  $339.4 \pm 0.5 \text{ kJ mol}^{-1}$  for the singlet together with an endothermicity of  $248 \text{ kJ mol}^{-1}$ . The triplet state lies much higher in energy.

The rate constants of carbene formation calculated from the G3 results over the temperature range 500–2000 K are given (in  $\text{s}^{-1}$ ) by

$$k_{\beta} = 9.48 \times 10^{13} \exp(-35\,230/T) \quad (1)$$

$$k_{\alpha} = 7.77 \times 10^{13} \exp(-41\,483/T) \quad (2)$$

Thus, reaction 2, methyl group transfer, only becomes significant at temperatures above 2000 K. Note that the rate of H-atom formation is comparable to  $\beta$ -carbene formation and is roughly 10 times faster at 2000 K.

**Fate of Carbenes.** The singlet  $\alpha$ -carbene formed by a methyl-group transfer dissociates to methyl acetylene and methyl ketene in a slightly exothermic process,  $\Delta H_f(298.15 \text{ K}) \approx -3.8 \text{ kJ mol}^{-1}$ , Figure 6; barriers of 124.0 (CBS-QB3) and 126.9 (G3)  $\text{kJ mol}^{-1}$  result.

Given the reaction enthalpy above we compute  $\Delta H_f(298.15 \text{ K}) = 125.4 \pm 3.5 \text{ kJ mol}^{-1}$  for the singlet  $\alpha$ -carbene of 25DMF based on propyne<sup>55</sup> and methylketene<sup>56</sup> values of  $185.21 \pm 0.69$  and  $-63.6 \pm 2.8$ , respectively.

The calculated rate constant is  $k = 7.24 \times 10^{14} \exp(-16\,417/T) \text{ s}^{-1}$  based on G3 energies and HF/6-31G(d) frequencies, rotational constants, and hindered rotor analysis. As a test, the same rate constant was computed but with CBS-QB3 energies and B3LYP/6-311G(d,p) data yielding  $k = 1.10 \times 10^{15} \exp(-16\,060/T) \text{ s}^{-1}$ . The G3-derived rate constants are therefore some 60% smaller than the CBS-QB3 ones over the entire temperature range, consistent with the previous example.

The comparable  $\alpha$ -carbene formed from a  $5 \rightarrow 4 \text{ H}$  shift in 2-methylfuran dissociates (to methyl acetylene and ketene) in a

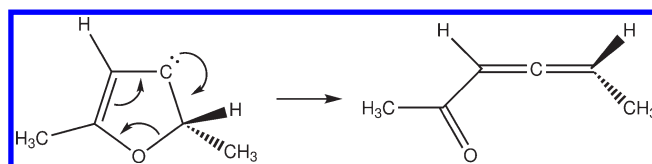
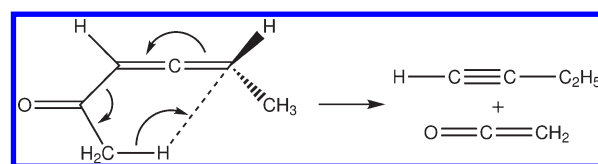
Figure 7. Decomposition of 25DMF  $\beta$ -carbene to *trans*-hexa-3,4-dien-2-one.

Figure 8. Fragmentation of hex-3,4-dien-2-one via a 1,5-H shift.

somewhat more exothermic reaction,  $-12.9 \pm 2.1 \text{ kJ mol}^{-1}$ , but has an essentially identical barrier of  $128.3 \pm 1.8 \text{ kJ mol}^{-1}$ .

The  $\beta$ -carbene can ring open to yield hexa-3,4-dien-2-one, a *trans* (OCCH  $180^\circ$ ) keto-allene, Figure 7, with a G3 barrier of approximately zero  $\text{kJ mol}^{-1}$ ; the comparable process in furan is barrierless.

The appropriate *cis* conformer (OCCH  $0^\circ$ ) of the keto-allene, Figure 8, can then fragment to butyne and ketene via a 1,5-H shift and a barrier of  $288.5 \pm 4.7 \text{ kJ mol}^{-1}$ ; a rate constant of  $5.20 \times 10^{13} \exp(-36\,800/T) \text{ s}^{-1}$  applies. Hence, the initial pyrolysis of 2,5-dimethylfuran should therefore result in the prompt formation of methylketene and propyne in 1:1 proportions and ketene and ethylacetylene (1-butyne) in a 1:1 ratio if thermal decomposition is routed through carbenes exclusively. In their speciation study of a 25DMF flame Wu et al.<sup>23</sup> did identify both ketenes and propyne but not butyne. Only the  $\text{C}_4\text{H}_6$  isomers 1,3-butadiene and cyclobutene are reported by them. The single-pulse shock tube study of Lifshitz et al.<sup>16</sup> did identify propyne and 1-butyne among the products but no ketenes, probably a reflection on the analytical technique used.

The *cis* conformer of hexa-3,4-dien-2-one ( $9.0 \pm 0.2 \text{ kJ mol}^{-1}$  more stable than the *trans*) has an enthalpy of formation of  $\Delta H_f(298.15 \text{ K}) = -10.0 \pm 2.9 \text{ kJ mol}^{-1}$  given a reaction enthalpy of  $127.0 \pm 1.0$ , Figure 8, and with known values of  $-48.2 \pm 2.6$  for ketene and  $165.2 \pm 0.9 \text{ kJ mol}^{-1}$  for ethylacetylene.<sup>57</sup>

Analogously, the  $\beta$ -carbene of 2-methylfuran, formed by a 3,2-H shift with a similar barrier to that in the analogous 25DMF case, ring opens to a keto-allene (*trans*-penta-3,4-dien-2-one) barrier, the *cis* conformer of which can then undergo a 1,5-H-shift and decompose to ketene + propyne with a barrier of  $284.3 \pm 4.8 \text{ kJ mol}^{-1}$ .

Huntsman and Yin<sup>58</sup> found that pyrolysis of 3,4-pentadien-2-one (1,2-pentadien-4-one or acetyllallene) at 706–793 K in a flow system led to a 72% yield of 2-methylfuran and speculated



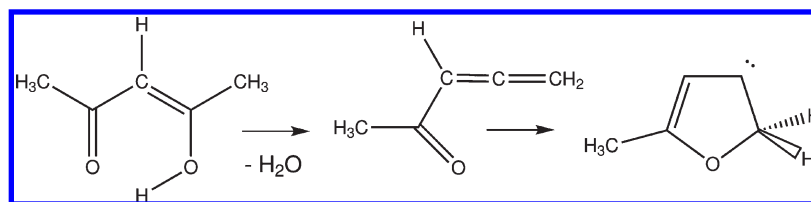


Figure 9. Formation of 2-methylfuran from acetylacetone.<sup>59</sup>

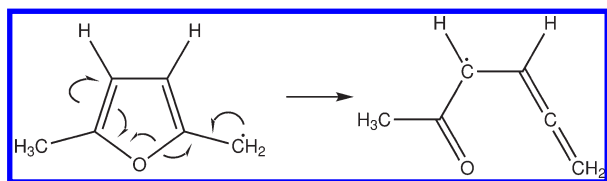


Figure 10. Ring opening of 25DMF2R radical.

that a  $\beta$ -carbene intermediate was involved. In laser-powered homogeneous pyrolysis experiments on acetylacetone (pentane-2,4-dione) Russel and Yee<sup>59</sup> reported 2-methylfuran as a major product. They considered that 2MF is formed from an intermediate acetyllallene produced by elimination of water from acetylacetone, Figure 9.

**5-Methyl-2-furanylmethyl Radical (25DMF2R).** Since the 5-methyl-2-furanylmethyl radical is almost certainly the most important species formed by hydrogen-abstraction reactions from the parent compound as well as directly by C–H scission, its reactions are of considerable interest. Note that 25DMF2R was detected by Wu et al.<sup>23</sup> on the basis of similarity between their measured ionization energy of 6.64 eV and their computed value of 6.59 eV (this work  $6.70 \pm 0.06$  eV), in low-pressure, rich, premixed laminar flames.

It has been postulated that ring opening proceeds by cleavage of the O–C bond, leading to endothermic formation of 4,5-hexadien-2-on-3-yl, and we can confirm that this process occurs with energy barriers of 164.0 and 154.4 kJ mol<sup>−1</sup> at CBS-QB3 and CBS-APNO, respectively, Figure 10. Although the transition state fails the T1 diagnostic test of Lee and Taylor,<sup>60</sup> a CASPT2(Se,So)/cc-pVDZ//B3LYP/6-311G-(d,p) calculation<sup>61</sup> yields a zero-point-corrected electronic energy of 169.6 kJ mol<sup>−1</sup>.

The calculated rate constant for ring opening is  $k = 8.50 \times 10^{13} \exp(-20\,320/T) \text{ s}^{-1}$ , based on the CBS-QB3 results; the half-life of 25DMF2R is thus approximately 5  $\mu\text{s}$  at 1000 K.

A heat of formation of  $\Delta H_f^\circ(298.15\text{ K}) = 135.6 \pm 6.4$  for the O=C–C–H 180° conformer shown in Figure 10 of 4,5-hexadien-2-on-3-yl follows from the calculated reaction enthalpy of  $124.0 \pm 2.6$  and a formation enthalpy of  $11.6 \pm 5.8$  for 25DMF2R.<sup>17</sup> This conformer is  $11.4 \pm 0.4$  kJ mol<sup>−1</sup> less stable than the OCCH 0° form, with an interconversion barrier of ca. 68 kJ mol<sup>−1</sup> at B3LYP/6-311G(d,p).

Sun and Wong<sup>62</sup> computed the energetics of ring-opening reactions of 2-furylcarbenes which bear some similarities to the current system; however, their G2(MP2,SVP) barriers are very low, ca. 8 kJ mol<sup>−1</sup>, for this strongly exothermic reaction, Figure 11.

Enlargement of the furan ring to give a six-membered heterocycle, Figure 12, is probably not significant since the reaction is endothermic by  $187.9 \pm 1.8$  kJ mol<sup>−1</sup>.

**2,5-Dimethyl-3-furanyl Radical (25DMF3R).** The other product of H-atom abstraction from the parent 25DMF,

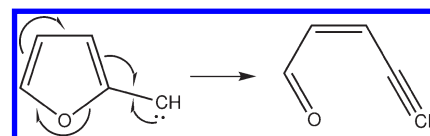


Figure 11. Ring opening of furylcarbene.<sup>62</sup>

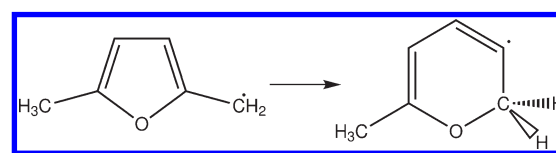


Figure 12. Ring enlargement.

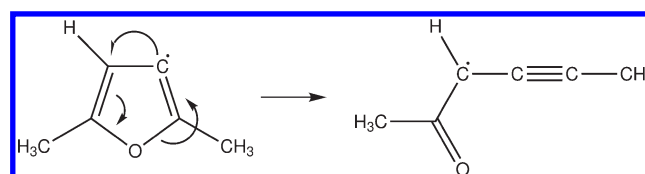


Figure 13. Ring opening of 25DMF3R radical to yield *trans*-2-hexyn-5-on-4-yl.

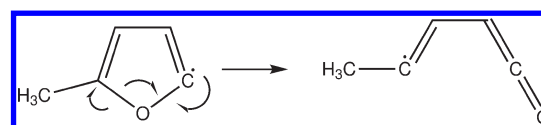


Figure 14. Ring opening of 2MF5R radical.

2,5-dimethylfuran-3-yl, was not observed at photoionization energies near 8.58 eV (this work  $8.53 \pm 0.07$  eV) by Wu et al. unsurprisingly given the very strong C–H bond. It can also ring open to yield a keto–alkyne radical (2-hexyn-5-on-4-yl), Figure 13, with a barrier of  $101.9 \pm 4.2$  kJ mol<sup>−1</sup> and  $k = 1.023 \times 10^{14} \exp(-13\,529/T) \text{ s}^{-1}$ . Identification of propenylketene however (see below) indicates that abstraction of a ring hydrogen does occur in low-pressure premixed 25DMF/O<sub>2</sub>/Ar flames even though the primary radical 25DMF3R is not itself observed probably because it lies below the detection limit.

The ring opening of 25DMF3R, Figure 13, has a reaction enthalpy at 298.15 K averaging to  $-29.8 \pm 4.1$  kJ mol<sup>−1</sup>; allied to a formation enthalpy of  $157.2 \pm 5.5$  for 25DMF3R<sup>17</sup> this implies  $\Delta H_f^\circ(298.15\text{ K}) = 127.4 \pm 6.9$  kJ mol<sup>−1</sup> for *trans*-2-hexyn-5-on-4-yl. The conformer with a dihedral angle for OCCH of 0° is  $7.0 \pm 0.5$  kJ mol<sup>−1</sup> more stable than the *trans* shown, and the interconversion barrier amounts to 44.2 kJ mol<sup>−1</sup>.

**2-Methyl-5-furanyl Radical (2MF5R).** The barrier for the ring-opening reaction of the monomethyl furan radical 2MF5R, Figure 14, ranges from 135.2, to 129.7, to 181.2 kJ mol<sup>-1</sup> at CBS-QB3, CBS-APNO, and G3 respectively. Although probably not significant in the context of the pyrolysis/oxidation of 2,5-dimethylfuran itself, it may play an important role in the pyrolysis/oxidation of 2-methylfuran and is therefore considered here. The results illustrate a potential pitfall with those multilevel methods which employ two geometry optimizations such as G3 and CBS-APNO. The first G3 optimization step finds a transition state, confirmed by the subsequent frequency calculation at HF/6-31G(d), in which, for example,  $r(\text{C}_2\text{—O}) = 2.081 \text{ \AA}$  and  $\angle(\text{C}_3\text{C}_4\text{C}_5) = 105.6^\circ$ , but the second optimization step, at MP2(full)/6-31G(d), leads to a quite different structure, now  $r(\text{C}_2\text{—O}) = 2.657 \text{ \AA}$  and  $\angle(\text{C}_3\text{C}_4\text{C}_5) = 118.7^\circ$ , which is not a transition state at the relevant level of theory, MP2(full)/6-31G(d). In the case of CBS-APNO the two optimized structures are substantially the same, for example,  $r(\text{C}_2\text{—O}) = 2.071$  and  $2.110 \text{ \AA}$  and  $\angle(\text{C}_3\text{C}_4\text{C}_5) = 105.2^\circ$  and  $103.4^\circ$ , and this probably accounts for the good agreement with the single-optimization method CBS-QB3. Hence, one would conclude that  $132.5 \pm 5.5 \text{ kJ mol}^{-1}$  probably represents the true barrier for this process, somewhat lower than for the comparable ring opening of the more stable 25DMF2R radical but somewhat higher than the ring opening of the less stable 2MF3R radical of  $111.0 \pm 2.6 \text{ kJ mol}^{-1}$ .

**Demethylation Reactions.** 4,5-Hexadien-2-on-3-yl, formed from the ring-opening reaction of 25DMF2R, can eliminate a methyl group to form 1,3,4-pentatrien-1-one (allenylketene C<sub>5</sub>H<sub>4</sub>O), Figure 15, with a barrier of  $207.9 \pm 2.1 \text{ kJ mol}^{-1}$  and a rate constant of  $1.313 \times 10^{15} \exp(-27235/T) \text{ s}^{-1}$ .

The fate of allenylketene may well involve decarbonylation to yield an unstable allenylcarbene,  $\text{H}\ddot{\text{C}}\text{—C}=\text{C}=\text{CH}_2$ , which can then isomerize to butatriene, vinylacetylene, and methylenecyclopropene as discussed by Aycard et al.<sup>63</sup> in their

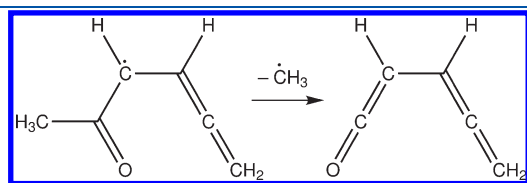


Figure 15. 4,5-Hexadien-2-on-3-yl to allenylketene.

photolytic study of matrix-isolated allenylketene. Allenylketene (this work  $8.18 \pm 0.05 \text{ eV}$ , cf. measured  $8.12 \text{ eV}$ , and calculated  $8.02 \pm 0.15 \text{ eV}$ <sup>23</sup>) and the C<sub>4</sub>H<sub>4</sub> isomers butatriene (this work  $9.14 \pm 0.042 \text{ eV}$ , cf. measured  $9.132 \text{ eV}$ , and computed  $9.15 \pm 0.02 \text{ eV}$ )<sup>23</sup> and vinylacetylene (this work  $9.58 \pm 0.032 \text{ eV}$ , cf. measured  $9.552 \text{ eV}$ ,<sup>23</sup> and lit.  $9.58 \text{ eV}$ <sup>48</sup>) were all identified by Wu et al. in their low-pressure premixed 25DMF flames.<sup>23</sup>

In a similar vein, the product from 25DMF3R ring opening, the 2-hexyn-5-on-4-yl radical, can eliminate methyl and form pent-1-en-3-yn-1-one,  $\text{O}=\text{C}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_3$  (propenylketene, this work  $8.40 \pm 0.01 \text{ eV}$ , also found by Wu et al., measured  $8.25 \text{ eV}$ , and calculated at  $8.19 \pm 0.15 \text{ eV}$ ) with a rate constant of  $2.00 \times 10^{14} \exp(-25776/T) \text{ s}^{-1}$ ; the barrier height at  $201.4 \pm 5.4 \text{ kJ mol}^{-1}$  is comparable to the previous case, as are the rate constants. Presumably, loss of CO would lead in a similar vein to a carbene,  $\text{H}\ddot{\text{C}}-\text{C}\equiv\text{C}-\text{CH}_3$ , which would also isomerize to butatriene, etc. Further study of these carbenes is complicated by their highly multiconfigurational character.<sup>63</sup>

## METHYL RADICAL ADDITION TO O=CXY

Many of the reactions considered here have not been the subject of experimental measurements, and hence, validation of the results obtained by computations is desirable. Consequently, we explored addition of methyl radical to the oxygen atom and the central carbon atom in a number of simpler compounds of general form  $\text{O}=\text{CXY}$  for which limited experimental and computational evidence exists. The results are shown in Table 1; as regards formaldehyde, Che et al.<sup>64</sup> have recently shown via CCSD(T)/6-311G(2df,p)//B3LYP/6-311+G(d,p) calculations that  $E(0 \text{ K}) + \text{ZPE}$  barriers of  $34.0$  and  $69.5 \text{ kJ mol}^{-1}$  for C- and O-atom-centered addition with reaction enthalpies of  $-38.1$  and  $-23.3 \text{ kJ mol}^{-1}$ , respectively, Table 2. The multilevel results obtained here are in moderate agreement with their computations and in reasonable agreement with measured and estimated activation energies.

Boyd and Boyd noted, in a study<sup>65</sup> of the addition and abstraction reactions of the methyl radical to aldehydes inter alia, that in general DFT, specifically B3LYP/6-31G(d), gives lower barriers and more exothermic reaction enthalpies than the G2 method. This is the case here too for CBS-QB3 and G3, see Tables 1 and 2. Paradoxically, this means that the methods are actually closer in agreement for the reverse barrier, that is, elimination of methyl from a radical. For

Table 1. Barriers for Methyl Addition to  $\text{O}=\text{CXY}$  (kJ mol<sup>-1</sup>)

species	CBS-QB3	CBS-APNO	G3	mean	lit.	$E_A/\text{kJ mol}^{-1}$
addition to carbon						
H <sub>2</sub> C=O	25.1	26.5	32.1	$27.9 \pm 3.7$	34.0 <sup>64</sup>	$25.1^{66} 26.5^{67} 33.0^{68}$
CH <sub>3</sub> HC=O	35.5	36.4	41.9	$37.9 \pm 3.5$	37 <sup>65</sup>	$35.5^{66} 38.7^{67} 39.3^{68}$
H <sub>2</sub> C=C=O	45.0	36.9	40.5	$40.8 \pm 4.1$	54–60 <sup>69</sup>	
CH <sub>3</sub> HC=C=O	37.7	36.8	36.3	$36.9 \pm 0.7$		
H <sub>2</sub> C=C=CHCH=C=O	26.7	25.4	37.8	$30.0 \pm 6.8$		
CH <sub>3</sub> C≡CHC=C=O	31.5					
addition to oxygen						
H <sub>2</sub> C=O	77.2	78.6	85.3	$80.4 \pm 4.4$	69.5 <sup>64</sup>	80 <sup>65</sup>
CH <sub>3</sub> HC=O	83.0	84.5	91.6	$86.4 \pm 4.6$		
H <sub>2</sub> C=C=O	113.3	114.7	121.0	$116.3 \pm 4.1$	126 <sup>69</sup>	
CH <sub>3</sub> HC=C=O	110.2	109.2	115.6	$111.7 \pm 3.5$		

**Table 2.** Forward Reaction Enthalpies  $\Delta H_r(0\text{ K})$  for Methyl Addition ( $\text{kJ mol}^{-1}$ )

species	CBS-QB3	CBS-APNO	G3	mean	lit.	$\Delta E^\ddagger(\text{rev.})$
addition to carbon						
$\text{H}_2\text{C}=\text{O}$	−42.4	−39.9	−37.4	$−39.9 \pm 2.5$	−38.1	$67.8 \pm 1.5$
$\text{CH}_3\text{HC}=\text{O}$	−19.5	−20.5	−14.4	$−18.1 \pm 3.3$	−16 <sup>65</sup>	$56.0 \pm 1.0$
$\text{H}_2\text{C}=\text{C}=\text{O}$	−125.5	−124.7	−117.2	$−122.4 \pm 4.6$		$163.3 \pm 6.6$
$\text{CH}_3\text{HC}=\text{C}=\text{O}$	−154.3	−153.7	−145.5	$−151.2 \pm 4.9$		$188.1 \pm 5.5$
$\text{H}_2\text{C}=\text{C}=\text{CHCH}=\text{C}=\text{O}$	−182.7	−180.1	−171.0	$−177.9 \pm 6.2$		$207.9 \pm 2.1$
$\text{CH}_3\text{C}\equiv\text{CHC}=\text{C}=\text{O}$	−175.2		−165.9			206.7
addition to oxygen						
$\text{H}_2\text{C}=\text{O}$	−29.6	−31.5	−24.6	$−28.6 \pm 3.6$	−23.3	$109.0 \pm 1.9$
$\text{CH}_3\text{HC}=\text{O}$	−16.1	−16.1	−9.4	$−13.9 \pm 3.9$	−12 <sup>65</sup>	$100.2 \pm 1.0$
$\text{H}_2\text{C}=\text{C}=\text{O}$	39.6	42.3	47.9	$43.3 \pm 4.2$		$73.1 \pm 0.6$
$\text{CH}_3\text{HC}=\text{C}=\text{O}$	27.7	30.1	36.2	$31.3 \pm 4.4$		$80.3 \pm 1.9$

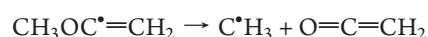
**Table 3.** Barriers to H Abstraction by OH

	$\Delta E^+ (0\text{ K})^a/\text{kJ mol}^{-1}$		
radical product	CBS-QB3	G3	ref
abstraction from furan ring			
DMF3R	21.5	35.3	
2MF3R	23.2	37.0	120.2 <sup>c</sup>
2MF4R	24.3	38.5	36.4 <sup>c</sup>
2MF5R	28.2	42.7	113.5 <sup>c</sup>
3MF2R	27.9	41.6	45.2 <sup>b</sup>
3MF4R	23.9	37.9	39.9 <sup>b</sup>
3MF5R	27.7	42.5	48.9 <sup>b</sup>
F2R	29.7	44.7	49.6 <sup>d</sup>
F3R		40.6	45.8 <sup>d</sup>
abstraction from methyl group			
DMF2R		15.5	
2MF2R		16.5	13.1 <sup>c</sup>
3MF3R		7.4	12.1 <sup>b</sup>

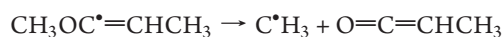
<sup>a</sup> Includes ZPE. <sup>b</sup> Average of G3MP2 and G3MP2B3.<sup>24</sup> <sup>c</sup> G3MP2B3 (298.15 K),<sup>25</sup> <sup>d</sup> G3MP270.

<sup>a</sup> Includes ZPE. <sup>b</sup> Average of G3MP2 and G3MP2B3. <sup>24</sup> <sup>c</sup> G3MP2B3 (298.15 K). <sup>25</sup> <sup>d</sup> G3MP270.

example, consider



The computed  $\Delta H^\ddagger(298.15\text{ K})$  are 74.7, 73.0, and 73.9  $\text{kJ mol}^{-1}$  for the CBS and G3 methods; a similar concordance is the case too for all the other C–O bond scissions and for C–C bond scission in  $\text{CH}_3\text{CH}_2\dot{\text{O}}$  and  $(\text{CH}_3)_2\text{CH}\dot{\text{O}}$  but is somewhat less convincing elsewhere, for example



with  $\Delta H^\ddagger(298.15\text{ K})$  of 193.6, 189.2, and 184.4  $\text{kJ mol}^{-1}$  resulting in a mean of  $189.1 \pm 4.6\text{ kJ mol}^{-1}$ .

However, it is possible to conclude that the barriers obtained for demethylation of 4,5-hexadien-3-yl-2-one to allenylketene, Figure 15, of  $207.9 \pm 2.1\text{ kJ mol}^{-1}$  and that for 2-oxo-hex-4-ynyl radical of  $201.4 \pm 5.4\text{ kJ mol}^{-1}$  are not unreasonable.

## H ABSTRACTION BY OH

H-abstraction reactions by the hydroxyl radical from 3-methylfuran have been studied by Zhang et al.;<sup>24</sup> they found that abstraction from the ring has barriers of 40–50  $\text{kJ mol}^{-1}$ , whereas abstraction from the methyl group has a barrier of 12  $\text{kJ mol}^{-1}$ . We expanded this work to consider abstraction from 2,5-dimethyl, 2- and 3-methyl furans, and furan itself for a total of 12 distinct cases, Table 3.

Although not all the transition states could be easily located, some general conclusions can be drawn from the data which both reinforces and extends the work by Zhang et al. on 3-methylfuran and 2-ethylfuran.<sup>26</sup> Abstraction barriers, reported as zero-point-corrected electronic energies,  $\Delta E^\ddagger(0\text{ K})$ , for hydrogens beside the heterocyclic O atom are all approximately the same and slightly higher, by about 5  $\text{kJ mol}^{-1}$ , than those for remote hydrogens, Figure 16. An increase in the number of  $-\text{CH}_3$  groups on the ring lowers the barriers for ring-C–H abstraction by a few  $\text{kJ mol}^{-1}$ . This parallels our previous finding<sup>17</sup> that ring-C–H bond dissociation energies are all effectively the same and are not influenced by the number or location of methyl groups.

Abstraction from the methyl groups have much lower barriers than from the ring, with abstraction from methyl group(s) remote from the O atom being lower by about 8  $\text{kJ mol}^{-1}$  than from methyls adjacent to the O atom. In contrast, the methyl C–H bonds are 17  $\text{kJ mol}^{-1}$  stronger when the methyl group is remote from the O atom.

The literature data for the  $\dot{\text{O}}\text{H} + 2\text{-methylfuran}$  system<sup>25</sup> at G3MP2B3 does seem to be somewhat anomalous since it does not fit with the  $\dot{\text{O}}\text{H} + 3\text{-methylfuran}$  results nor with reasonable expectations. For example, although the barrier for abstraction from the methyl group is very similar to that for 3-methylfuran, abstraction from the ring carbons varies widely, Figure 17. Consequently, we carried out G3MP2B3 computations of the reactions leading to formation of the three different 2-methylfuryl radicals, 2MF3R, 2MF4R, and 2MF5R, and find zero-point-corrected electronic energy barriers of 34.6, 38.1, and 42.3  $\text{kJ mol}^{-1}$ , respectively. These results are now in concordance with those for the formation of 3-methylfuryl radicals and with our own CBS-QB3 and G3 results.

Although the CBS-QB3 barriers are substantially lower than the computed G3 ones, Table 3, exactly the same conclusions emerge. Note that the CBS-QB3 model chemistry uses a B3LYP functional and a CBSB7 or 6-311G(2d,d,p) basis set as the

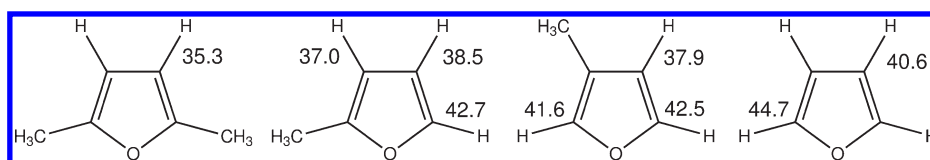


Figure 16. Barriers, G3 (0 K), to H-atom abstraction by  $\dot{\text{O}}\text{H}$  radical.

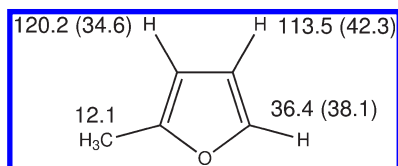


Figure 17. Barriers, G3MP2B3 (0 K), to H-atom abstraction by  $\dot{\text{O}}\text{H}$  radical (this work).

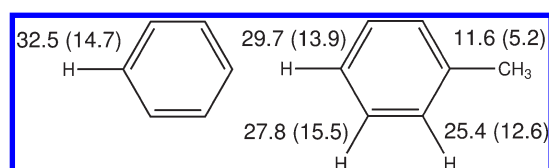


Figure 18. Barriers, G3MP2B3 (0 K), to H-atom abstraction by  $\dot{\text{O}}\text{H}$  radical<sup>71</sup> (CBS-QB3).

geometrical optimizer; this combination can have convergence problems and appears to be particularly acute for those transition states leading to formation of furfuryl radicals. Zhang et al.<sup>25</sup> reported a similar difficulty in locating the transition state, leading to formation of the 2-methylfurfuryl radical with B3LYP/6-311G(d,p) failing but B3LYP/6-31G(d) succeeding.

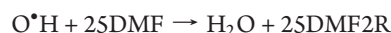
Finally, the recent transition state theory calculations of Mousavipour et al.<sup>70</sup> on  $\dot{\text{O}}\text{H}$  + furan at different levels of theory, including MP2, CCSD, MPWB1K, CCSD(T), and G3MP2, show that the barrier height for abstraction from the 2 position is always slightly greater than that from the 3 position, Table 3. Thus, the data for the furans is internally consistent and a clear picture emerges, but in order to put the above results into context we also consider H abstraction from the prototypical aromatics, benzene, and toluene by  $\dot{\text{O}}\text{H}$ .

Seta et al.<sup>71</sup> reported energy barriers for abstraction from benzene and the toluene ring at CBS-QB3 and G3MP2B3, respectively, see Figure 18. The barriers for abstraction from the ring carbons are higher for the furans than the benzenes, possibly reflecting the stronger ring-C–H bond in the furans over those in the benzenes. Methylation of the aromatic benzene or furan rings decreases the H-atom abstraction barriers in both cases; proximity to the methyl group is not a major influence. Abstraction from the methyl group in toluene was correspondingly lower at 5.2 and 11.6 kJ mol<sup>−1</sup> at CBS-QB3 and G3MP2B3.

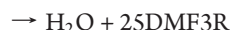
Of course, reactions of the  $\dot{\text{O}}\text{H}$ ,  $\text{H}\dot{\text{O}}_2$ , and similar radicals are more varied than the above computations would indicate. For example, formation of pre- and postreaction complexes is a common feature in the reactions of  $\dot{\text{O}}\text{H}$  with 2-ethylfuran,<sup>26</sup> ozone,<sup>72</sup> C1–C4 alcohols,<sup>73</sup> methyl ethers,<sup>74</sup> ketones,<sup>75</sup> benzene,<sup>76</sup> and hydroxyl and hydroperoxyl with butanol,<sup>77,78</sup> and these complications are also exhibited in the alkylfuran +  $\dot{\text{O}}\text{H}$  reactions considered here; Figure 19 represents one such interaction where the prereaction complex lies 18.5 kJ mol<sup>−1</sup> below the reactants. Although such complexes are both interesting and

of particular importance at lower temperatures (Galano and Alvarez-Idaboy<sup>79</sup> tabulate binding energies ranging from −13 to −31 kJ mol<sup>−1</sup> for a series of  $\dot{\text{O}}\text{H}$ -radical complexes with oxygenated volatile organic compounds) they were not pursued further here except to note that 2SDMF... $\dot{\text{O}}\text{H}$  shares some similarities with the benzene... $\dot{\text{O}}\text{H}$  complex, Figure 20, which is 15.1 kJ mol<sup>−1</sup> more stable than the isolated reactants.

Finally, the rate constants for H abstraction from the ring carbons and the methyl side chain, calculated from G3 results and with no account taken of prereactive complexes, can be summarized as



$$k = 1.016 \times 10^4 T^{3.133} \exp(-1085/T) \text{ s}^{-1}$$



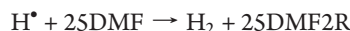
$$k = 3.93 \times 10^4 T^{2.668} \exp(-3871/T) \text{ s}^{-1}$$

Thus, even at the highest temperature of 2000 K abstraction from the ring is of limited significance.

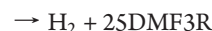
## H-ABSTRACTION AND ADDITION REACTIONS

Hydrogen-atom abstraction by H atoms shares some similarities with abstraction by  $\dot{\text{O}}\text{H}$ ; thus, the G3 barriers for the exothermic (−78.5 kJ mol<sup>−1</sup>) abstraction from the methyl group of 29.5 kJ mol<sup>−1</sup> are considerably lower than from the ring carbon of 87.9 kJ mol<sup>−1</sup>, which is endothermic by 65.3 kJ mol<sup>−1</sup>. Similar conclusions apply for the other abstracting species, Table 4. For 2-methylfuran the H-abstraction reaction barriers and endothermicities are very similar to those for 2SDMF; for 2MF there are three kinds of ring-carbon H atoms, but it transpires that there is very little difference in either barriers, 90 ± 2 kJ mol<sup>−1</sup>, or enthalpy change, 66 ± 2 kJ mol<sup>−1</sup>, for these abstraction sites.

The rate constants computed from the G3 results for 2SDMF are



$$3.86 \times 10^5 T^{2.679} \exp(-2683/T) \text{ s}^{-1}$$



$$7.78 \times 10^7 T^{2.002} \exp(-10156/T) \text{ s}^{-1}$$

Thus, as is also the case with abstraction by  $\dot{\text{O}}\text{H}$ , only at temperatures much in excess of 2000 K is H abstraction from the ring carbons beginning to make an impact on the reactivity of the molecule. Note too that  $\dot{\text{O}}\text{H}$  is much more reactive than H.

Abstraction from the methyl group by a H atom gives rise to a chiral transition state (categorized by Multiwell<sup>36</sup> as the number of 'optical isomers'), which can be transformed into its enantiomer by internal rotation; however, in this case, the number of optical isomers in the computation must be reduced to 1 if the internal rotation of the methyl group whose hydrogen is being abstracted is treated as an unsymmetrical hindered rotor.<sup>80</sup>



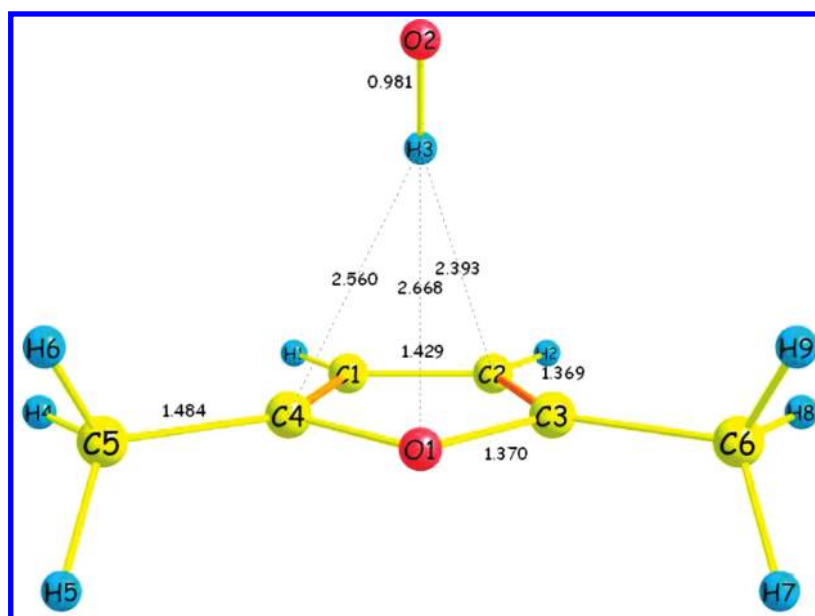


Figure 19. Prereaction complex formed by 2SDMF +  $\dot{\text{O}}\text{H}$ ; G3 geometry  $\angle \text{OHO} = 117.6^\circ$ .

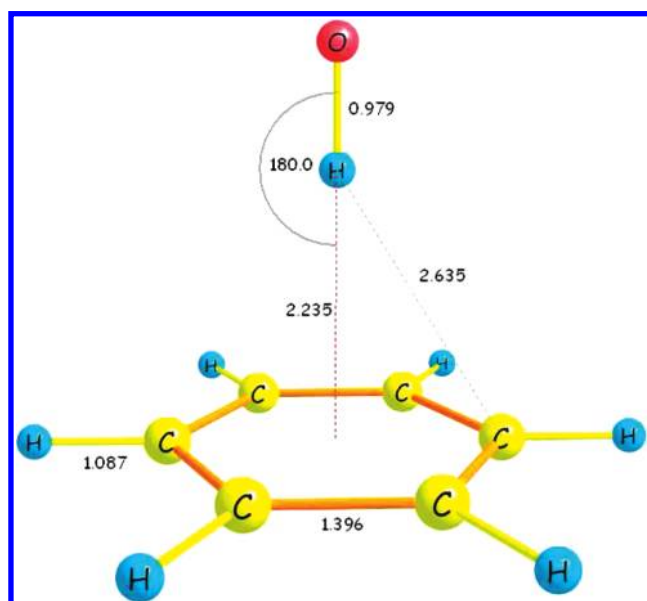


Figure 20. Prereaction complex formed by benzene +  $\dot{\text{O}}\text{H}$ ; G3 geometry.

Table 4. H Abstraction by  $\dot{\text{X}}$  from  $\text{CH}_3$  in 2SDMF ( $\text{kJ mol}^{-1}$ )

	G3 (0 K) barrier	G3 (0 K) reaction $\Delta H$
$\dot{\text{O}}\text{H}$	15.5	-133.1
$\dot{\text{H}}$	29.5	-78.5
$\text{HO}_2$	57.2	-2.1
$\dot{\text{O}}$	11.7	-72.1
$\dot{\text{C}}\text{H}_3$	52.7	-73.2

Although this second approach is more correct it requires scans not just of the potential energy as a function of the dihedral but also of the moment of inertia and is therefore much more

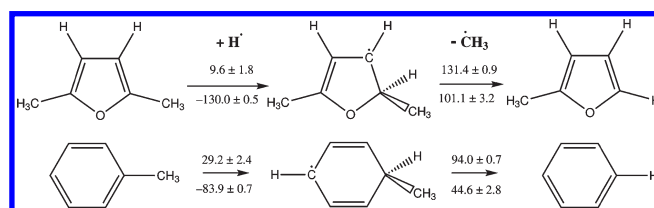


Figure 21. H-atom addition and methyl elimination; 0 K barriers and reaction energies  $\text{kJ mol}^{-1}$ .

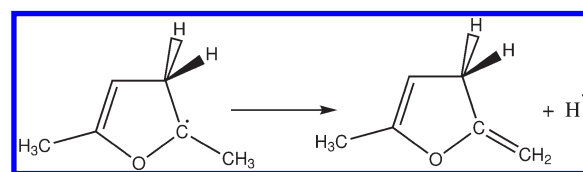


Figure 22. Formation of 2,3-dihydro-5-methyl-2-methylenefuran.

laborious. Fortunately, it makes very little difference to the computed rate constant which of these methods is used.

Addition of a hydrogen atom to the furan ring at a methyl site is feasible and indeed faces a lower barrier (G3) of  $7.6 \text{ kJ mol}^{-1}$ ; the resultant radical, 2SDMF2H3R, can then eliminate the methyl group, Figure 21, to form 2-methylfuran, which was one of the products identified by Wu et al. in 2,5-dimethylfuran flames.<sup>23</sup> It was also the only oxygenated product observed in the thermal decomposition of 2SDMF behind reflected shock waves.<sup>16</sup> The rate constant for H addition at C2 is given by  $k = 8.84 \times 10^8 T^{1.507} \exp(-782.7/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ; thus, this reaction is faster than H abstractions even from the methyl groups for temperatures below 1500 K. Elimination of methyl has a rate constant of  $1.974 \times 10^{14} \exp(-16469/T) \text{ s}^{-1}$ . Direct cleavage of a methyl–ring bond in 2SDMF resulting in a 2-methyl-5-furanyl radical which could then form 2-methylfuran is unlikely given the  $480 \text{ kJ mol}^{-1}$   $\text{C}=\text{CH}_3$  bond strength.

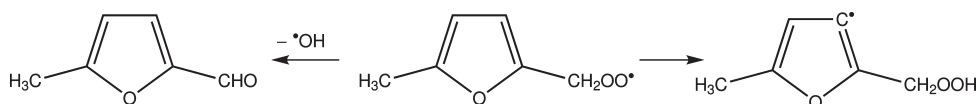
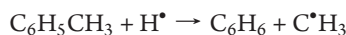


Figure 23. Reactions of peroxy radical, 5-methyl-2-furanmethylhydroperoxyl.

This addition–elimination sequence is also possible for 2-methylfuran as the energetics are very similar viz. H addition to form the 2MF2H radical  $7.53 \times 10^{8.7} T^{1.511} \exp(-955.83/T) \text{ cm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}$  followed by methyl elimination  $2.232 \times 10^{14} \exp(-16292/T) \text{ s}^{-1}$ . Of course, this and the previous sequence should be treated as chemically activated processes, but this is outside the scope of this work.

A similar addition/elimination process is known in the toluene system for which Kislov and Mebel<sup>81</sup> determined, from G3(MP2, CC)//B3LYP calculations, a barrier of 32.6 and a heat of reaction at 0 K of  $-73.2$  for the addition step and  $90.8$  and  $37.2 \text{ kJ mol}^{-1}$  for the methyl elimination. The comparable values using the three composite methods employed in this work are  $29.2 \pm 2.4$  and  $-83.9 \pm 0.7$  for H addition and  $94.0 \pm 0.7$  and  $44.6 \pm 2.8 \text{ kJ mol}^{-1}$ , Figure 21, for methyl elimination. Note that estimated activation energies for the reaction



range from  $33.8$  to  $21.5 \text{ kJ mol}^{-1}$ .<sup>82–84</sup> At high temperatures and low pressures the theoretical calculations and estimates are not therefore in conflict.

Addition of H at a ring carbon to yield 2,3-dihydro-5-methyl-2-methylfuran, Figure 22, is also feasible given barriers of  $16.1 \pm 0.8 \text{ kJ mol}^{-1}$  and an exothermicity of  $-86.0 \pm 0.7 \text{ kJ mol}^{-1}$ . The addition reaction is actually faster than either H-abstraction reactions. The ensuing fate of this radical is less clear; one possibility is elimination of a H atom from the methyl group at the C5 position to form 2,3-dihydro-5-methyl-2-methylenefuran, Figure 22. This compound is less stable by  $\Delta H_f(298.15 \text{ K}) = 70.3 \pm 3.7 \text{ kJ mol}^{-1}$  than its isomer 25DMF, in agreement with an earlier DFT study.<sup>85</sup> A rate constant for the H-addition reaction of  $2.03 \times 10^9 T^{1.439} \exp(-1395/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  can be calculated directly, while that for the H elimination of  $6.02 \times 10^{14} \exp(-19736/T) \text{ s}^{-1}$  is computed via the reverse reaction.

In a similar vein, OH addition at C(2) leads to a radical of 2,3-dihydro-2,5-dimethyl-2-furanol which can either ring open yielding 5-hydroxy-4-hex-3-yl-2-one with a barrier of  $78.1 \text{ kJ mol}^{-1}$  or alternatively eliminate methyl to give 2-methyl-5-furanol with a barrier of  $162.8 \text{ kJ mol}^{-1}$ . Zhang et al.<sup>25</sup> noted that attack of OH at the C2 position in 2-methylfuran is a barrierless association, giving rise to an adduct at  $132.5 \text{ kJ mol}^{-1}$  below the reactants at G3MP2B3, and that this can ring open (barrier  $76.8 \text{ kJ mol}^{-1}$ ) or eliminate methyl with a barrier  $152.5 \text{ kJ mol}^{-1}$ ; similar values to those found here.

**Reaction with O<sub>2</sub>.** Addition of oxygen to the benzyl radical is a well-known reaction in toluene oxidation,<sup>86–91</sup> so we considered the reaction of oxygen with the dominant radical 25DMF2R leading to hydroperoxide formation and elimination of hydroxyl as two possible outcomes, Figure 23. The 25DMF2R–O<sub>2</sub> adduct lies  $68.6 \pm 2.4 \text{ kJ mol}^{-1}$  below the reactants; the benzyl–O<sub>2</sub> adduct lies  $93.3 \text{ kJ mol}^{-1}$  below the reactants.<sup>89</sup>

The endothermic formation of the hydroperoxide proceeds via a six-center transition state with  $\Delta G^\ddagger(0 \text{ K})$  of  $184.8 \text{ kJ mol}^{-1}$  and  $k = 2.83 \times 10^{12} \exp(-22534/T)$ , whereas elimination of OH and formation of the aldehyde is somewhat higher at

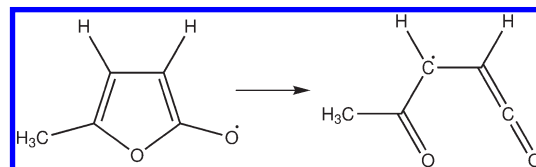


Figure 24. Ring opening of 5-methyl-2-furanyloxy.

$195.3 \text{ kJ mol}^{-1}$  with an exothermicity of  $-127.1 \text{ kJ mol}^{-1}$  and  $k = 1.46 \times 10^{13} \exp(-24192/T) \text{ s}^{-1}$ .

These values are not wholly dissimilar to the benzyl–O<sub>2</sub> system of  $136$  and  $162 \text{ kJ mol}^{-1}$ , respectively, obtained in a comprehensive CBS-QB3 study by Murakami et al.<sup>89</sup> They showed that dissociation of the adduct back to reactants is the dominant channel with those channels leading to formation of benzaldehyde + OH and a hydroperoxide radical of much lesser importance; indeed, the channel in which O adds to the ring carbon with a barrier of  $128 \text{ kJ mol}^{-1}$  forming a 1,2-dioxetane is of considerably greater importance,  $\sim 10^4$ , but still does not rival back dissociation. The comparable reaction in this system would lead to formation of a furanyloxy radical, Figure 24, and elimination of formaldehyde; the barrier to this process is considerably lower at  $102 \text{ kJ mol}^{-1}$  than the other two channels.

An estimate of the back dissociation rate of  $1.31 \times 10^{20} T^{-1.987} \exp(-9544/T) \text{ s}^{-1}$  can be obtained by assuming that the rate of 25DMF2R + O<sub>2</sub> is equal to the rate of benzyl + O<sub>2</sub>, taken to be a constant<sup>89</sup>  $2.63 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and from the computed equilibrium constant. Therefore, the findings of Murakami et al. regarding the relative importance of the channels open to C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OO are mirrored in this dimethylfuran system. It is perhaps not surprising therefore that Wu et al. did not detect any compounds containing 2 or more oxygen atoms in their VUV-MBMS flame study.

Interestingly, the ring opening of the 5-methyl-2-furanyloxy radical is a relatively facile process with a barrier of  $82 \text{ kJ mol}^{-1}$  at G3, yielding a radical of keteneacetone or 1-penten-3-yl-1,4-dione, Figure 24, which can then demethylate to form 1,4-dioxo-1,3-butadiene, a bisketene.

## CONCLUSIONS

The pyrolytic behavior of 25DMF arises from a competition between production of H atoms by scission of the CH<sub>2</sub>–H bond and formation of a β-carbene by a 3,2-H-shift. The formation and destruction reactions of H atoms during the early stages of the pyrolysis process are explored as are several of the ring-opening steps.

A consistent picture emerges for the reaction barriers for H-atom abstraction from methyl-substituted furans by OH and other species H, CH<sub>3</sub>, etc. Addition of radicals to the furan double bond emerges as a potent channel and most clearly explains formation of 2-methylfuran from the parent 2,5-dimethylfuran observed in flames and shock tube experiments by an addition–elimination sequence.<sup>16,23</sup>

We show that identification of 2-ethenylfuran (2-vinylfuran) as an C<sub>6</sub>H<sub>6</sub>O intermediate in rich 2,5-dimethylfuran flames is

probably not correct and is more likely to be, on the basis of calculated ionization energies, the isomeric 2,5-dimethylene-2,5-dihydrofuran.

There is clearly a considerable amount of work remaining to be done since most of the intermediate species reported here have a largely unknown chemistry (even the relatively simple ketoallene shown in Figure 7, hexa-3,4-dien-2-one, is absent from the American Chemical Society databases CAplus and CAS Registry), and in addition, there is a dearth of relevant experiments.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Table of calculated rate constants and geometries, frequencies, hindered rotor barriers, and energetics of most species, including transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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