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Primary Combustion Intermediates in Lean and Rich Low-pressure Premixed Laminar 2-Methylfuran/Oxygen/Argon Flames

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ABSTRACT

Combustion intermediates in low-pressure premixed laminar 2-methylfuran/oxygen/argon flames with equivalence ratios of 0.8 and 1.5 were investigated by using tunable synchrotron vacuum ultraviolet photoionization and molecular-beam mass spectrometry. 2-Methylfuran (MF) is a promising biofuel with great potentials of being used in different fields including the auto industry. However, the combustion chemistry of MF is not clear. Photoionization mass spectra of

MF/oxygen/argon flames were recorded as well as the photoionization efficiency curves (PIEs) of the combustion intermediates. Ionization energies (IEs) were measured from the PIEs. The combustion intermediates were identified by comparing the measured IEs with those reported in the literatures or calculated with the method of *ab initio*. Possible reaction pathways of MF and its primary combustion derivatives were constructed based on the combustion intermediates identified. H-abstraction and the consecutive reaction products were identified, including furfural, (*Z*)-1-oxo-1,3,4-pentatriene, 2-ethylfuran, and 2-vinylfuran, etc. 2-Oxo-2,3-dihydrofuran was also observed, which may originate from the OH addition products on the furan ring. Furan was not observed in the low-pressure MF flames. Substituted ketenes, (*Z*)-1-oxo-1,3,4-pentatriene and (*E*)-1-oxo-1,3-butadiene, were both detected in the low-pressure MF flames.

TEXT

1. INTRODUCTION

Furan and its derivatives, 2-methylfuran (MF) and 2,5-dimethylfuran (DMF), are new kind of biofuels. DMF can be produced from biomass such as fructose, glucose, or even cellulose.[1-3] In making DMF, MF will also be produced. Besides, MF can be produced even from hemicellulose. MF has a higher research octane number (RON) than DMF has (131 vs. 119)[1]. MF is simpler than DMF with only one methyl side chain on the furan ring. Studying the combustion of MF will also help in clarifying the combustion process of DMF.

There are some early studies on the thermal decomposition of furan series biofuels by Grela et al.[4] and Lifshitz et al.[5-7] Recently, the combustion of furan series biofuels has attracted more attention. Some of the recent works include the low-pressure experimental studies by Wu et al.[8] and Tian et al.[9], and the theoretical studies by Zhang et al.[10] and Simmie et al.[11]

Wu et al.[8] studied the low-pressure premixed laminar flame of DMF. By identifying the combustion intermediates, reaction pathways of DMF and its derivatives were analyzed, including those of MF. Due to the similarity in the structures of DMF and MF, they always produce the same primary derivatives in flames. This will complicate the analysis of the combustion of DMF and MF. Tian et al.[9] identified MF in their low-pressure premixed laminar furan flame. They provided some elementary reactions for MF. No oxygenated products of MF were reported in their experiments.

In their theoretical study of the reaction of OH with MF, Zhang et al.[10] focused on all possible product channels, and provided the probable reaction pathways. Their results lacked the support of experimental results. In their theoretical study of the decomposition of DMF, Simmie et al.[11] pointed out the initial steps of the reactions of DMF. They also calculated the energy barriers of H-abstraction of MF by OH. According to their results, H-abstraction on the methyl side chain dominates the consumption of MF.

A more recent study of the oxidation of MF was reported by Somers et al[12]. They combined the experimental studies of ignition delay times as well as laminar burning velocities and theoretical study with a detailed chemical kinetic model to study the combustion characteristics of MF. In their rate of production analysis of the shock tube conditions, over 30% of MF were consumed by H-abstractions to form 2-furanylmethyl at 20% fuel consumption. No contribution from the oxygenation and radical combination of 2-furanylmethyl was reported to the consumption of this radical at this point.

The experimental results of low-pressure premixed laminar MF/oxygen/argon flames with equivalence ratios of 0.8 (lean flame) and 1.5 (rich flame) are presented here, combining the technologies of ultra-violet vacuum synchrotron radiation photoionization and molecular-beam mass spectroscopy. Combustion intermediates were identified by comparing the measured ionization energies (IEs) with those reported in the literature. Based on the combustion intermediates detected, possible primary reaction pathways of MF were constructed. This will help in constructing the combustion reactions of MF, as well as in reducing the detailed mechanism.

2. EXPERIMENTAL SETUP

The experiments were carried out on the Combustion and Flame Endstation in the National Synchrotron Radiation Laboratory, Hefei, China. The instruments have been reported elsewhere.[13] In brief, it consisted of a low-pressure flame chamber, a molecular-beam flame-sampling system, and a photoionization chamber with a reflectron time-of-flight mass spectrometer. A steady MF/oxygen/argon flame was formed in the flame chamber, which consisted of a fuel and oxidizer mixture supply system, a 6.0-cm-diameter McKenna burner and a pressure monitoring and controlling system. Combustion intermediates were sampled at selected position by a quartz nozzle with an orifice of about 500 μm in diameter at the tip in the molecular-beam flame-sampling system. After being collimated by a nickel skimmer upon entering the photoionization chamber, the combustion intermediates were ionized by the tunable synchrotron radiation and detected by the mass spectrometer. Resolution of the mass spectrometer was about 1500. Intensity of the ion signal and time of flight were recorded by a computer.

The flow rates of MF (purity ⩾ 99%) as well as those of oxygen (O_2) and argon (Ar) in the experiments are listed in Table 1. The pressure in the flame chamber was maintained at 30 Torr (4.0 kPa). The temperature of the vaporizer was maintained at 150 °C to ensure sufficient evaporation of MF (boiling point, 63 °C[1]). Flow rate of the liquid fuel was controlled by a syringe pump (ISCO Inc., USA), while those of gases were controlled by mass flow controllers (Multi Gas Controller 647 C, MKS Instruments Inc., USA).

By scanning the wavelength of the synchrotron radiation, the photoionization efficiency curves (PIEs) were recorded at the sampling position (distance from the tip of the sampling quartz nozzle to the burner surface) of 5.5 mm and 3.0 mm for the rich flame and the lean flame, respectively. At these positions, most combustion intermediates had relatively higher ion intensities. IEs of the corresponding combustion intermediates were measured from the PIEs. Given the cooling effect of the molecular-beam and the energy resolution of the monochromator, the experimental error bars of the measured IEs were ± 0.05 eV for the combustion intermediates with strong signal-to-noise (S/N) ratios and ± 0.10 eV for those with poor S/N ratios. By comparing with the IEs reported in literatures or those calculated, the structures of the combustion intermediates were identified. IEs of the possible combustion intermediates were calculated in case of the absence of literature values. Geometries and energies of the possible combustion intermediates and their ions were computed at *ab initio* Gaussian-03 (G3) level. The error bars of the calculated IEs are within ± 0.15 eV.

3. RESULTS AND DISCUSSION

3.1. Flame mass spectra

Figures 1a and 1b show the series of mass spectra for the lean and the rich MF flames, respectively. The mass spectra were taken at the photon energy of 11.00 eV and at various sampling positions. The number of mass peaks in the lean flame is basically the same as that in the rich flame. But the heights of these peaks are different in the two flames. The mass peaks can roughly be categorized into seven groups, with each group centering on *m*/*z* = 15, 28, 40, 54, 68, 82, and 96, respectively. These seven groups can be roughly denoted as C1, C2, C3, C4, C5/C4O, C6/C5O, and C6O/C5O2 in the case of MF flames, respectively. The highest mass peak appears in the C6/C5O group at *m*/*z* = 82 in both flames, since this signal mainly originates from the fuel molecules. In the lean flame, the maximum height of the mass peaks decreases in the order of C2, C3, C4, and C5/C4O, while in the rich flame, the maximum height of the mass peaks in the C2, C3, and C4 groups are roughly at the same level.

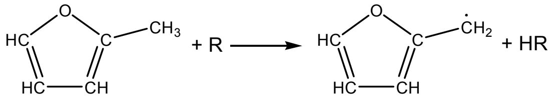
Even the relative mass peaks' heights in a single group will change with varying the sampling position. The signals at *m*/*z* = 50, 52, and 54 in the C4 group of the rich flame is a good example, as shown in Figure 1b. Before the sampling position of 5 mm, the mass peak of *m*/*z* = 54 is higher than those of *m*/*z* = 52 and *m*/*z* = 50. Between the sampling position of 6 mm and 7 mm, the mass peak of *m*/*z* = 52 becomes the dominant one. While at the sampling position of 8 mm, the mass peak of *m*/*z* = 50 is absolutely higher than the other two mass peaks. This is an interesting phenomenon that the three signals dominate one by one with the increase of the sampling position.

3.2. H-abstraction of MF

3.2.1. Formation and reactions of 2-furylmethyl

Calculated chemical structure of MF ($C_4H_3OCH_3$, *m*/*z* = 82) at G3B3 level is shown in Figure 2a, together with the corresponding bond lengths and bond energies. In the molecule of MF, the bond energy of C(6)–H is much lower than that of C(2)–C(6) and those of C–H on the furan ring.

Thus, C(6)–H is more easily broken in the combustion of MF to form 2-furylmethyl ($C_4H_3OCH_2$, $m/z = 81$),



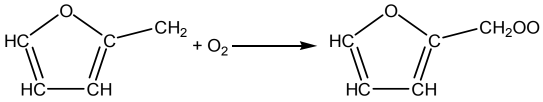
(R1)

where R may be OH, H, O, or O_2, etc. in R1 and in the following reactions, with HR being H_2O, H_2, OH, or HO_2, etc., correspondingly. IE of 2-furylmethyl was calculated to be 7.05 eV. Clear onsets at 7.08 eV can be observed in the PIEs of the combustion intermediates of $m/z = 81$, as shown in Figure 3a. This onset is the IE of this combustion intermediate. The calculated IE of 2-furylmethyl agrees well with the experimental IE of the combustion intermediates of $m/z = 81$. This experimental value is also in excellent agreement with the previously reported one of 7.05 eV by Wu et al.[8] As concluded by Simmie et al.,[11] H-abstraction from the furan ring is of limited significance. H-abstraction from the methyl side chain accounts for the formation of this radical detected in MF flames. With an extensively delocalized structure, as shown in Figure 2b, the low IE value measured for this radical is reasonable.

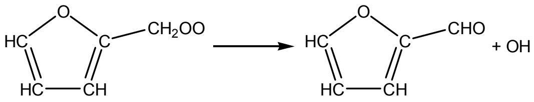
Oxidation of 2-furylmethyl. Once formed, 2-furylmethyl may react with the ambient oxygen molecules. The conjugated structure of this radical bears some similarity with that of benzyl ($C_6H_5CH_2$). As reported by Murakami et al.,[14] reaction of benzyl with oxygen molecule mainly leads to the formation of benzaldehyde,

$$C_6H_5CH_2 + O_2 \rightarrow C_6H_5CHO + OH \qquad \text{(R2a)}$$

Similarly, 2-furylmethyl may also react with oxygen molecule to form furfural (C_4H_3OCHO, $m/z = 96$) in the flame,



(R3)



(R4a)

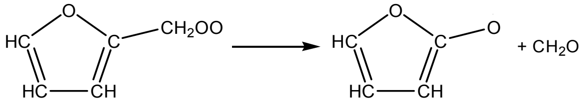
IE of furfural was reported in literature as 9.22 eV.[15] This value is slightly lower than the calculated value, 9.26 eV. Figure 3b shows the PIE of the combustion intermediates of $m/z = 96$. In the lean flame, an onset at 9.35 eV can be observed. The calculated IE of furfural is slightly lower than the experimental value, but still lies in the experimental error bar.

The onset around the photon energy of 9.35 eV in the rich flame is not so obvious than that in the lean flame. This can be attributed to the weakened oxygenation (R3) in the rich flame. Weak onset corresponding to the IE of furfural in the rich flame is in accordance with the experimental results of Wu et al.[8] Onset corresponding to the IE of the oxidized product of 5-methylfurfural ($CH_3C_4H_3OCHO$) was not observed in their richer DMF flame ($\phi = 2.0$).

Reaction of benzyl with oxygen molecule may also lead to the formation of phenoxyl (C_6H_5O) and formaldehyde,

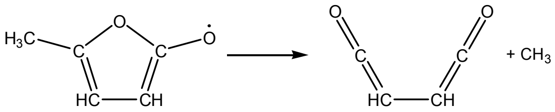
$C_6H_5CH_2 + O_2 \rightarrow C_6H_5O + CH_2O$ (R2b)

Analogous reaction of 2-furylmethyl with oxygen molecule may also lead to the similar products, 2-furyloxyl and formaldehyde,



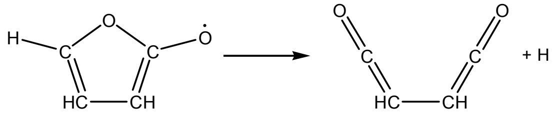
(R4b)

2-Furyloxyl is not stable. According to an analogous reaction of 5-methyl-2-furanyloxyl and subsequent reaction supposed by Simmie et al.,[11]



(R5)

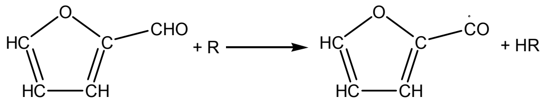
2-furyloxyl may also turn into 1,4-dioxo-1,3-butadiene (O=C=CH–CH=C=O, m/z = 82) in a similar way,



(R6)

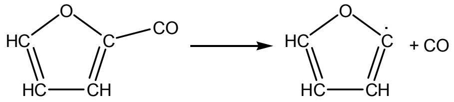
IE of 1,4-dioxo-1,3-butadiene was calculated to be 8.15 eV and 8.01 eV for the (*Z*)- and (*E*)-form, respectively. But no obvious onset can be observed below the photon energy of 8.41 eV in the PIEs of the combustion intermediates of m/z = 82, as shown in Figure 3c. Two obvious onsets can be observed in these PIEs at 8.41 eV and 10.05 eV, respectively. The lower onset at 8.41 eV agrees well with the IE of MF, 8.38 eV, reported in literature[15]. Calculated IE of MF at G3B3 level, 8.43 eV, also agrees well with this value. The higher onset at 10.05 eV agrees well with the higher ionization potential of MF, reported to be 10.03 eV[16]. Absence of the onset corresponding to the IE of 1,4-dioxo-1,3-butadiene can either be attributed to the low branching ratio to R4b or to the very strong signal of the fuel molecules. As concluded by Murakami et al.[14], branching ratio of the reaction of benzyl with oxygen leading to phenoxyl and formaldehyde, R2b, is about 20%.

Analogous to the fate of benzaldehyde, H-abstraction from the formyl group should account for most of the consumption of furfural. This will lead to the formation of 2-furoyl,



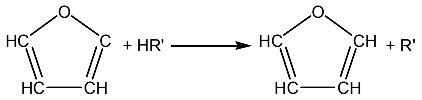
(R7)

2-Furoyl is not stable. It will decompose into 2-furyl and carbon monoxide,



(R8)

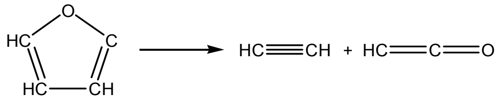
Theoretically, 2-furyl may abstract a hydrogen atom from other molecules to form furan (C_4H_4O, $m/z = 68$),



(R9a)

HR' can be HO_2, CH_4, or C_3H_4, etc. in R9a, with R' being O_2, CH_3, or C_3H_3, etc., correspondingly. Figure 3d shows the PIE of the combustion intermediates of $m/z = 68$. The only clear onset that can be observed is at 8.46 eV. This value is far from the literature IE of furan, 8.88 eV.[15] Wu et al.[8] detected furan in their DMF flame. They concluded that furan can be formed via R9a. In this work, high-purity MF was used as the fuel. The onset at 8.46 eV corresponds to the IE of (*E*)-1-oxo-1,3-butadiene, calculated to be 8.43 eV. Thus, R9a is likely not so important in the low-pressure combustion of MF. The unstable 2-furyl radical formed in R8 must be consumed via other reactions.

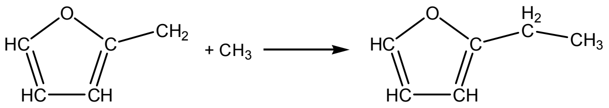
Structure of 2-furyl is shown in Figure 2c. By eliminating the methene side chain, the bond length of O(1)–C(2) decreases from 1.405 Å in 2-furylmethyl to 1.334 Å in 2-furyl, while that of O(1)–C(5) increases from 1.312 Å in 2-furylmethyl to 1.384 Å in 2-furyl. This suggests that the next reaction should be the further shortening of O(1)–C(2) and the further elongating of O(1)–C(5). Following this trend, the final result should be the breakage of O(1)–C(5) and C(3)–C(4) to decompose into acetylene and ketenyl,



(R9b)

Tian et al.[9] concluded that 2-furyl is completely consumed via this reaction.

Radical combination. Wu et al.[8] supposed that 2-furylmethyl may combine with CH_3 to form 2-ethylfuran ($C_4H_3OCH_2CH_3$, $m/z = 96$),

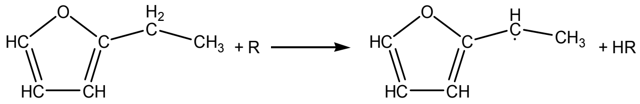


(R10)

IE of this molecule was reported to be 8.45 eV,[15] as compared with the calculated value of 8.36 eV. Obvious onsets at 8.37 eV can be observed in the PIEs of the combustion intermediates of *m*/*z* = 96, as shown in Figure 3b. This value agrees well with the literature value and the calculated one. Wu et al.[8] have not identified 2-ethylfuran in their DMF flame. One possible reason lies in the fact that the fuel they used was DMF. The strong signal of the fuel dwarfed that of 2-ethylfuran.

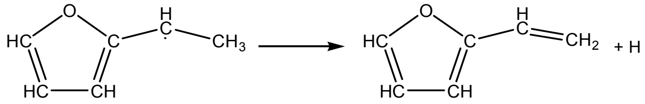
It is obvious that R10 competes with R3 in consuming 2-furylmethyl. In a lean flame where oxygen molecules are more abundant, R3 will be enhanced, while in a rich flame where CH_3 are more abundant, R10 will be enhanced. This competition between R10 and R3 will lead to the difference in the shape of the PIEs of 2-ethylfuran (*m*/*z* = 96) and furfural (*m*/*z* = 96), as shown in Figure 3b. The ion intensities of the signals in the rich and the lean flames are scaled to roughly the same level. It can be seen that the onset corresponding to 2-ethylfuran are sharper in the rich flame than that in the lean flame, while that corresponding to furfural are clearer in the lean flame than that in the rich flame. However, the ratio of 2-ethylfuran to furfural will change even in a single flame with the change of the sampling position. Quantitative results should provide with more details about the two combustion intermediates.

Given the lower bond energy of the C–Hs on the methene group, 2-ethylfuran might be consumed by H-abstraction to form 1-(2-furyl)ethyl,



(R11)

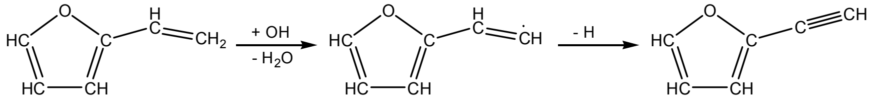
As supposed by Wu et al.,[8] 1-(2-furyl)ethyl may turn into 2-vinylfuran ($C_4H_3OC_2H_3$, $m/z = 94$) by H-fission,



(R12)

Simmie et al.[11] reported that IE of 2-vinylfruan was calculated to be 8.12 eV for the (*Z*)- and (*E*)-form. A clear onset at 8.12 eV can be observed in the PIE of the combustion intermediates of $m/z = 94$ in Figure 3e. The experimental IE agrees very well with that of 2-vinylfuran calculated. Wu et al.[8] reported an onset at 7.95 eV in the PIE of the combustion intermediates of $m/z = 94$ in their DMF flame. They attributed this onset to the IE of 2-vinylfuran. Simmie et al.[11] pointed out that this onset corresponds to the calculated IE of 2,5-dimethylene-2,5-dihydrofuran at 7.95 eV.

Analogous to the reactions of styrene[17], further H-abstraction of 2-vinylfuran may lead to the formation of 2-furylacetylene (C_4H_3OCCH, $m/z = 92$),

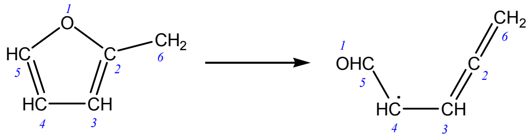


(R13)

IE of 2-furylacetylene was calculated to be 8.56 eV. No onset around this energy in the PIEs of the combustion intermediates of $m/z = 92$ can be observed. The only obvious onsets observed in these PIEs are at 8.79 eV, corresponding to the literature IE of toluene, 8.828 eV.[15] Absence of 2-furylacetylene can be attributed either to the weak signal, or to the low branching ratio from 2-vinylfuran to this combustion intermediate.

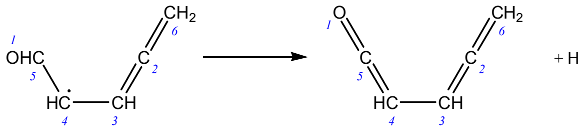
Combination products of 2-furylmethyl with radicals that have more carbon atoms were not detected, probably due to the short lifetime and hence low concentrations of the radicals, even with the rather stable propargyl radical and 2-furylmethyl itself.

Ring rupture. As shown in Figure 3b, the onsets corresponding to the IEs of furfural and 2-ethylfuran are not very clear even in the lean MF flame. This suggests that direct oxidation of 2-furylmethyl (R3) and radical combination (R10) cannot account for most of the consumption of 2-furylmethyl, especially in the rich flame. This is in accordance with the result of Somers et al.[12] In their rate of production analysis of MF under shock tube conditions, no obvious contribution from R3 and R10 were shown at 20% fuel consumption. There should be other reactions competing with R3 and R10. As can be seen in Figure 2c, upon losing a hydrogen atom from the methyl side chain, the bond length of O(1)–C(2) increased from 1.371 Å in MF to 1.405 Å in 2-furylmethyl, and that of O(1)–C(5) decreased from 1.366 Å in MF to 1.312 Å in 2-furylmethyl. O(1)–C(2) was elongated in the reaction from MF to 2-furylmethyl, while O(1)–C(5) was shortened. Following this trend, 2-furylmethyl may isomerize to form 3,4-pentadienaldehyde-2-yl (CH_2=C=CH–C·H–CHO) by further elongation and the breakage of O(1)–C(2), as discussed by Wu et al.,[8]



(R14)

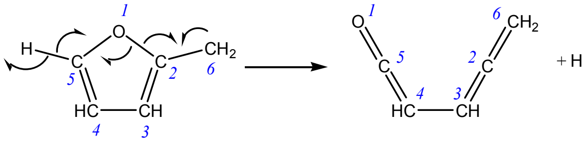
By H-fission, this radical may turn into (*Z*)-1-oxo-1,3,4-pentatriene ($m/z = 80$),



(R15)

PIEs of the combustion intermediates of $m/z = 80$ are shown in Figure 3f. A clear onset can be observed at 8.17 eV in the PIE of the rich flame and at 8.25 eV in that of the lean flame. Both values agree well with the calculated IE of (*Z*)-1-oxo-1,3,4-pentatriene, 8.19 eV. No other obvious onsets can be observed in these PIEs. Other possible H-fission products of 3,4-

pentadienaldehyde-2-yl were also considered, as shown in Figure 4, together with the corresponding IEs. Of these possible H-fission products, only the IE of (*Z*)-1-oxo-1,3,4-pentatriene agrees well with the experimental values. Onset corresponds to the calculated IE of (*E*)-1-oxo-1,3,4-pentatriene, 7.90 eV, was not observed. This implies that during the H-fission of 2-furylmethyl, C(2) and C(5) remain at the "same side" of the C(3) and C(4) bond. Thus, formation of (*Z*)-1-oxo-1,3,4-pentatriene from 2-furylmethyl probably carries out in a "direct" manner, i.e., in one step,



(R16)

In R16, the hydrogen atom on C(5) is abstracted. It is probably due to the slightly lower bond energy of this bond than that of C(3)–H and C(6)–H, as calculated by Simmie et al.,[11] that formation of (*Z*)-1-oxo-1,3,4-pentatriene is favored.

In Figure 3f, the onset in the rich flame is slightly lower than that in the lean flame. This can be attributed to the stronger signals in the rich flame. Stronger signals yield a smoother PIE, and thus a clearer onset.

Fate of 2-furylmethyl includes the oxidation to furfural and the decomposition to carbon monoxide (CO) and 1,3-butadien-1-yl (*n*-C_4H_5) according to the combustion mechanism for MF of Somers et al. At 20% fuel consumption in their shock tube experiment, reaction of 2-furylmethyl completely led to the formation of CO and *n*-C_4H_5. Detailed chemistry of 2-furylmethyl should also include radical combination (R10) and ring rupture reactions (R16). Reactions of (*Z*)-1-oxo-1,3,4-pentatriene may lead to CO and *n*-C_4H_5.

3.2.2. Other H-abstraction products of MF

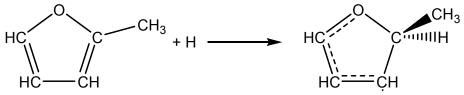
Products of H-abstraction from the ring carbons will always lead to the rupture of the furan ring. Detailed reaction pathways can be found elsewhere.[8]

3.3. Radical addition to MF

Radical addition may also contribute to the consumption of MF. Theoretically, OH may add onto any carbon atoms in the furan ring. Zhang et al.[10] reported that addition of OH on C(2) and C(5) were more favorable thermodynamically. In fact, addition onto C(2) or C(5) will lead to resonantly stabilized radicals.

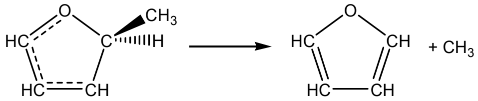
3.3.1. H addition

H addition onto C(2) will lead to the formation of 2,3-dihydro-2-methyl-3-furyl,



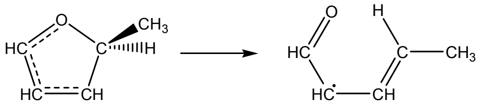
(R17a)

Analogous to the reaction between toluene and H, this radical may lead to the formation of furan and methyl,



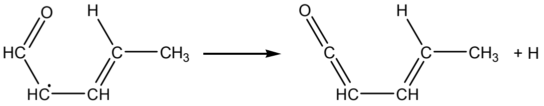
(R18a)

Since furan is not detected in the flame, as described in the previous section, R18a is likely not so important under low pressure. 2,3-Dihydro-2-methyl-3-furyl may turn into 3-pentenaldehyde-2-yl by breaking O(1)–C(2),

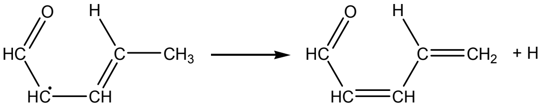


(R18b)

By H-fission, this radical may turn into 1-oxo-1,3-pentadiene (m/z = 82) or 2,4-pentadienaldehyde (m/z = 82),



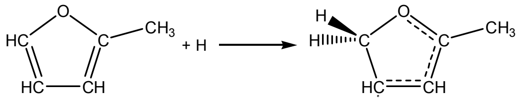
(R19a)



(R19b)

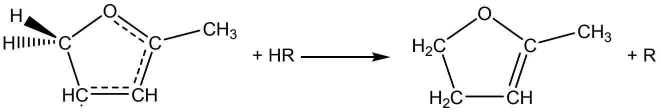
IE of 1-oxo-1,3-pentadiene were calculated to be 8.08 eV and 7.38 eV for the (*Z*)- and (*E*)-form, respectively. IE of 2,4-pentadienaldehyde were calculated to be 9.38 eV and 9.56 eV for the (*Z*)- and (*E*)-form, respectively. No obvious onsets corresponding to the calculated IEs can be observed in the PIE of the combustion intermediates of $m/z = 82$. This can be attributed either to the strong signals of the fuel molecules or to the low branching ratio of R18b.

H addition onto C(5) will lead to the formation of 4,5-dihydro-2-methyl-4-furyl, as supposed by Wu et al.,[8]



(R17b)

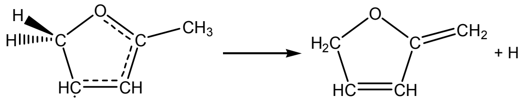
This radical may turn into 4,5-dihydro-2-methylfuran ($m/z = 84$) by abstracting an H atom from other molecules,



(R20a)

IE of 4,5-dihydro-2-methylfuran are calculated to be 8.04 eV. As can be seen in Figure 5, two onsets at 8.41 eV and 9.35 eV can be observed in the PIEs of the combustion intermediates of $m/z = 84$. The calculated IE is far from the experimental values. Thus R20a might not be an important reaction in the combustion of MF.

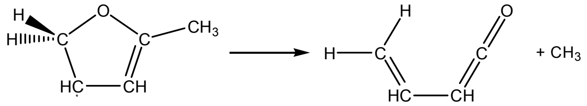
4,5-Dihydro-2-methyl-4-furyl may also turn into 2,5-dihydro-2-methylenefuran ($m/z = 82$), by H-fission from the methyl side chain,



(R20b)

IE of 2,5-dihydro-2-methylenefuran is calculated to be 9.72 eV. As can be seen in the PIEs of the combustion intermediates of m/z = 82, shown in Figure 3c, no obvious onset can be observed around 9.72 eV. Again this can be attributed either to the low branching ratio to this product, or to the very strong signal of the fuel molecules. There should be other reactions competing with R20a and R20b.

In fact, 4,5-dihydro-2-methyl-4-furyl may be consumed by the breakage of O(1)–C(5) and C(2)–C(6) to turn into 1-oxo-1,3-butadiene (CH_2=CH–CH=CO, m/z = 68),

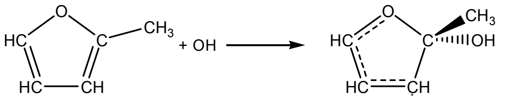


(R20c)

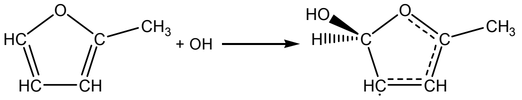
IE of (*E*)-1-oxo-1,3-butadiene is calculated to be 8.43 eV. This value agrees very well with the experimental one measured in the PIE of the combustion intermediates of m/z = 68, 8.46 eV, as shown in Figure 3d. It is obvious that the reaction pathway of R17b and R20c competes with that of R17a and R18a. Both reaction pathways lead to the formation of the combustion intermediates of m/z = 68, (*E*)-1-oxo-1,3-butadiene and furan, respectively. Observation of only the onset corresponding to the IE of (*E*)-1-oxo-1,3-butadiene indicates that the reaction pathway of R17b and R20c dominates over that of R17a and R18a. This is in accordance with the results of Somers et al.[12]

3.3.2. OH addition

As calculated by Zhang et al.[10] at the G3MP2B3 level, OH addition to MF was a barrierless process, comparing with the barrier of 13.11 kJ·mol^{-1} of H-abstraction process,

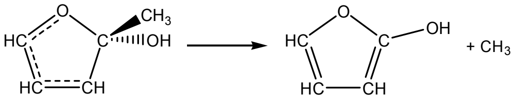


(R21a)



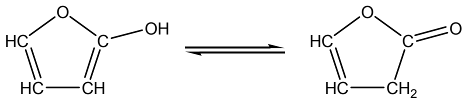
(R21b)

According to the analogous reaction of toluene and OH, R21a may lead to 2-hydroxylfuran ($m/z = 84$),



(R22a)

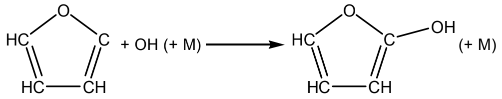
IE of 2-hydroxylfuran was calculated to be 8.17 eV and 8.20 eV for the (*Z*)- and (*E*)-form, respectively. As can be seen in Figure 5, two onsets can be observed in the PIEs of the combustion intermediates of $m/z = 84$. Scaled PIE of the fuel ($m/z = 82$) are also displayed in this figure for comparison. The lower onset at 8.41 eV corresponds to the IE of the isotope-abundant fuel molecule. The higher onset at 9.35 eV is close to the IEs of cyclopentanone and 1-hexene, reported to be 9.26 eV and 9.44 eV[15], respectively. Since no cyclopentane was observed in the flame, cyclopentanone cannot be a likely combustion intermediate here. Since no 1-pentene was observed in the lean flame, 1-hexene cannot be a possible in the lean flame, also. Another candidate to this combustion intermediate can be 2-oxo-2,3-dihydrofuran, with a calculated IE of 9.31 eV. An IE of 10.70 eV was reported for this species[15]. In fact this reported value was that of 2-oxo-2,5-dihydrofuran in literature[18] and agrees excellently with the calculated value of 10.70 eV at G3B3 level. 2-Oxo-2,3-dihydrofuran might isomerizes from 2-hydroxylfuran,



(R23a)

As can be seen that 2-hydroxylfuran is an enol. Enols are not stable chemically. They may turn into the more stable keto tautomer, as described in literature[19].

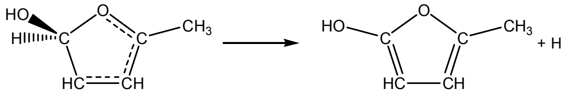
Theoretically, combination of 2-furyl and hydroxyl may also lead to the formation of 2-hydroxylfuran,



(R24)

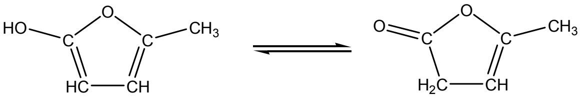
Since similar formation of furan (R9a) is not likely, R24 is also not likely to be an important pathway. According to Tian et al.[9], reaction of 2-furyl completely led to the decomposition products of acetylene and ketenyl (R9b). Reaction pathway of R21a and R22a may account for the formation of 2-hydroxylfuran.

Similarly, R21b may lead to the formation of 5-hydroxyl-2-methylfuran (*m*/*z* = 98),



(R22b)

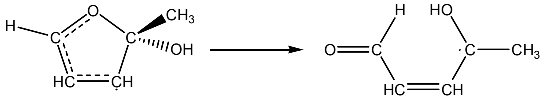
IE of 5-hydroxyl-2-methylfuran was calculated to be 7.78 eV and 7.80 eV for the (*Z*)- and (*E*)-form, respectively. No obvious onsets can be observed in the PIEs of the combustion intermediates of *m*/*z* = 98 around 7.78 eV, as shown in Figure 6. Analogous to the reaction of 2-hydroxylfuran, 5-hydroxyl-2-methylfuran may turn into 2-oxo-2,3-dihydro-5-methylfuran,



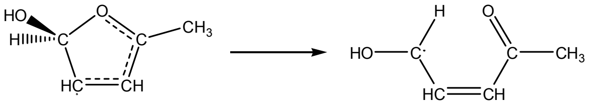
(R23b)

Thorstad et al.[20] reported an IE of 9.62 eV for 2-oxo-2,3-dihydro-5-methylfuran. They noticed that their reported IE was somewhat higher than the expected value. They concluded that their sample was tautomerized partially into 2-oxo-2,5-dihydro-5-methylfuran. IE of this latter molecule was reported to be 10.12 eV[20]. This value agrees very well with the calculated one, 10.06 eV. IE of 2-oxo-2,3-dihydro-5-methylfuran is calculated to be 8.92 eV. An obvious onset at 9.02 eV can be observed in the PIE of the combustion intermediates of *m*/*z* = 98 in the lean flame, as shown in Figure 6. No obvious onset can be observed around 8.92 eV in the PIE of the same combustion intermediate in the rich flame. This difference in the onset around 8.92 eV in the PIEs of the combustion intermediates of *m*/*z* = 98 between the lean flame and the rich flame coincides with that of 2-oxo-2,3-dihydrofuran. As can be seen in Figure 5, onset of 2-oxo-2,3-dihydrofuran is more obvious in the lean flame than that in the rich flame. Onset of 2-oxo-2,3-dihydrofuran is more obvious than that of 2-oxo-2,3-dihydro-5-methylfuran. This indicates that R21a might be more competitive than R21b be.

The addition products of R21a and R21b may also turn into 4-hydroxy-2-pentenal-5-yl and 5-hydroxy-3-penten-2-on-5-yl, respectively, as supposed by Zhang et al.[10],

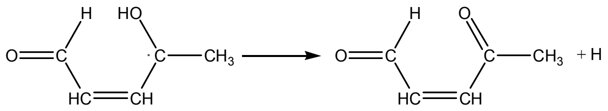


(R25a)

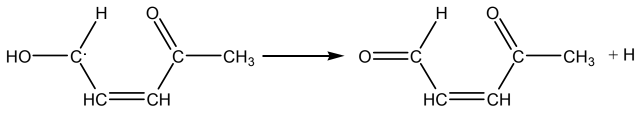


(R25b)

Both radicals may turn into (1*E*, 2*Z*, 3*Z*)-4-oxo-2-pentenal (*m*/*z* = 98) by H-fission from the OH group,



(R26a)

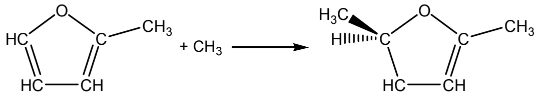


(R26b)

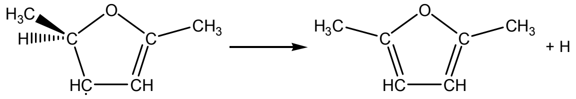
IE of (1*E*, 2*Z*, 3*Z*)-4-oxo-2-pentenal is calculated to be 9.33 eV. This value agrees well with the onset at 9.35 eV of the combustion intermediates of *m*/*z* = 98. This product was also observed by Gómez Alvarez et al.[21] The lower onsets in the PIE of the combustion intermediates of *m*/*z* = 98 might come from the enol-form of this carbonyl compound. Enols have been observed in many flames.[19, 22]

3.3.3. CH_3 addition

In the PIE of the combustion intermediates of *m*/*z* = 96, as shown in Figure 3b, the lower onset at 7.96 eV corresponds to the adiabatic IE of DMF, 8.03 eV. Observation of DMF is verified by the onset around 8.14 eV, which corresponds to its vertical IE. DMF can be formed by the addition of CH_3 onto C(5) in MF, via 2,3-dihydro-2,5-dimethyl-3-furyl,

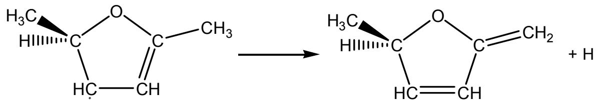


(R27)



(R28a)

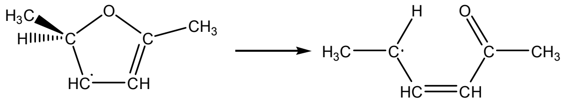
2,3-Dihydro-2,5-dimethyl-3-furyl may also turn into 2,5-dihydro-5-methyl-2-methylenefuran,



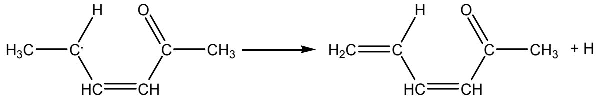
(R28b)

IE of 2,5-dihydro-5-methyl-2-methylenefuran was calculated to be 8.08 eV. This value is very close to the IE of DMF. Since ΔH_f(298.15 K) of 2,5-dihydro-5-methyl-2-methylenefuran was reported to be 70.3 kJ·mol^{-1} higher than that of DMF[11], R28a might not be so competitive as R28b be.

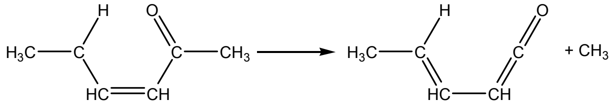
Another possible consumption pathway of 2,3-dihydro-2,5-dimethylfuran-3-yl might be the breakage of the C–O bond to form 3-hexen-2-on-5-yl,


(R28c)

This radical may turn into 3,5-hexadien-2-one (*m*/*z* = 96) by H-fission,


(R29a)

or turn into 1-oxo-1,3-pentadiene (*m*/*z* = 82) by losing a methyl,


(R29b)

IEs of 3,5-hexadien-2-one and 1-oxo-1,3-pentadiene are calculated to be 9.18 eV and 8.08 eV, respectively. Since no onsets can be observed in the respective PIEs of the combustion intermediates of *m*/*z* = 96 and *m*/*z* = 82 near the calculated IEs, as can be seen in Figure 3b and Figure 3c, respectively, these pathways might contribute little to the consumption of MF.

Primary reaction pathways of MF are summarized in Figure 7. Combustion intermediates identified in the lean and the rich MF flames are listed in Table 2. Common combustion intermediates with *m*/*z* < 60 are not listed here.

4. **CONCLUSIONS**

Primary combustion intermediates in the low-pressure premixed laminar rich and lean MF/oxygen/argon flames are identified. The primary reaction pathways of MF are constructed based on the primary combustion intermediates identified.

By H-abstraction, MF can be consumed to turn mainly into 2-furylmethyl. Then, 2-furylmethyl can further be consumed by oxidation, H-abstraction, and radical combination reactions. Oxidation of 2-furylmethyl leads to the formation of furfural. H-abstraction of 2-furylmethyl leads to the formation of (*Z*)-1-oxo-1,3,4-pentatriene. Combination of MF with CH_3 leads to the formation of 2-ethylfuran.

By radical addition, MF can also be consumed. H addition leads to the formation of 1-oxo-1,3-butadiene. OH addition leads to the formation of 2-oxo-2,3-dihydrofuran, 2-oxo-2,3-dihydro-5-methylfuran and (1*E*, 2*Z*, 3*Z*)-4-oxo-2-pentenal. CH_3 addition leads to the formation of 2,5-dimethylfuran.

Formation of ketene and substituted ketenes, (*Z*)-1-oxo-1,3,4-pentatriene and (*E*)-1-oxo-1,3-butadiene might be the feature of MF flames.

Furan combustion might not be so important in the combustion of MF. Combustion mechanism of MF should include that of DMF and *vice versa*.

FIGURES

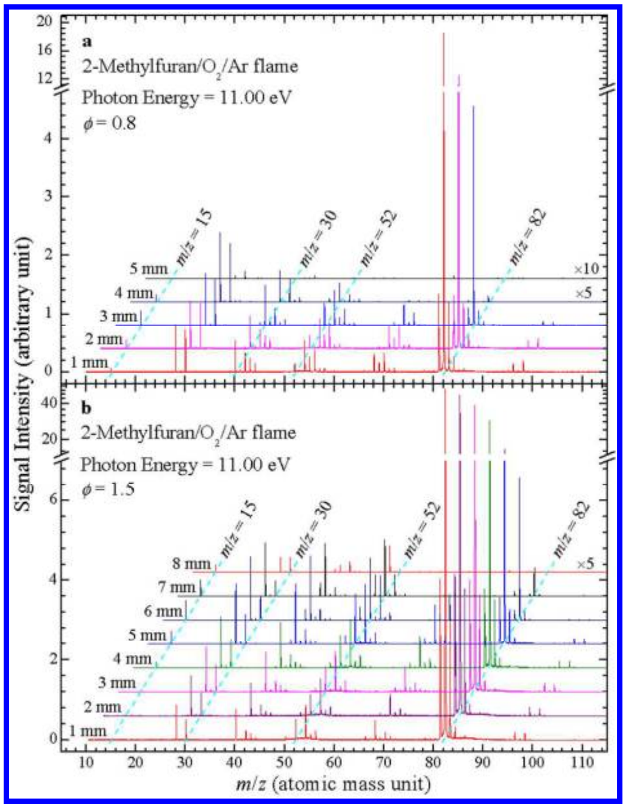


Figure 1. Mass spectra of the MF/O$_2$/Ar flame (Photon energy, 11.00 eV; equivalence ratio, a = 0.8, b = 1.5).

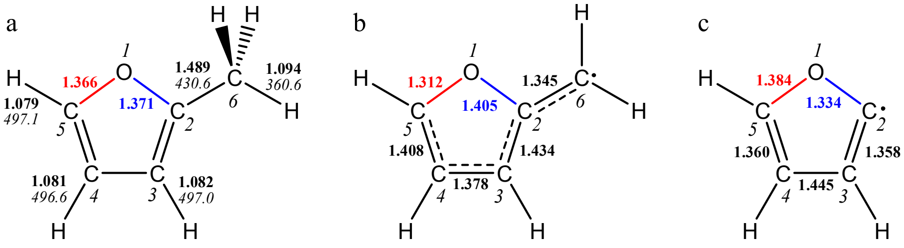


Figure 2. Calculated chemical structures of (a) MF, (b) 2-furylmethyl, and (c) 2-furyl at G3B3 level (bold value near the bond, bond length, in Å; italicized value near the bond, bond energy, in kJ·mol^{-1}; number near the atom, atom label).

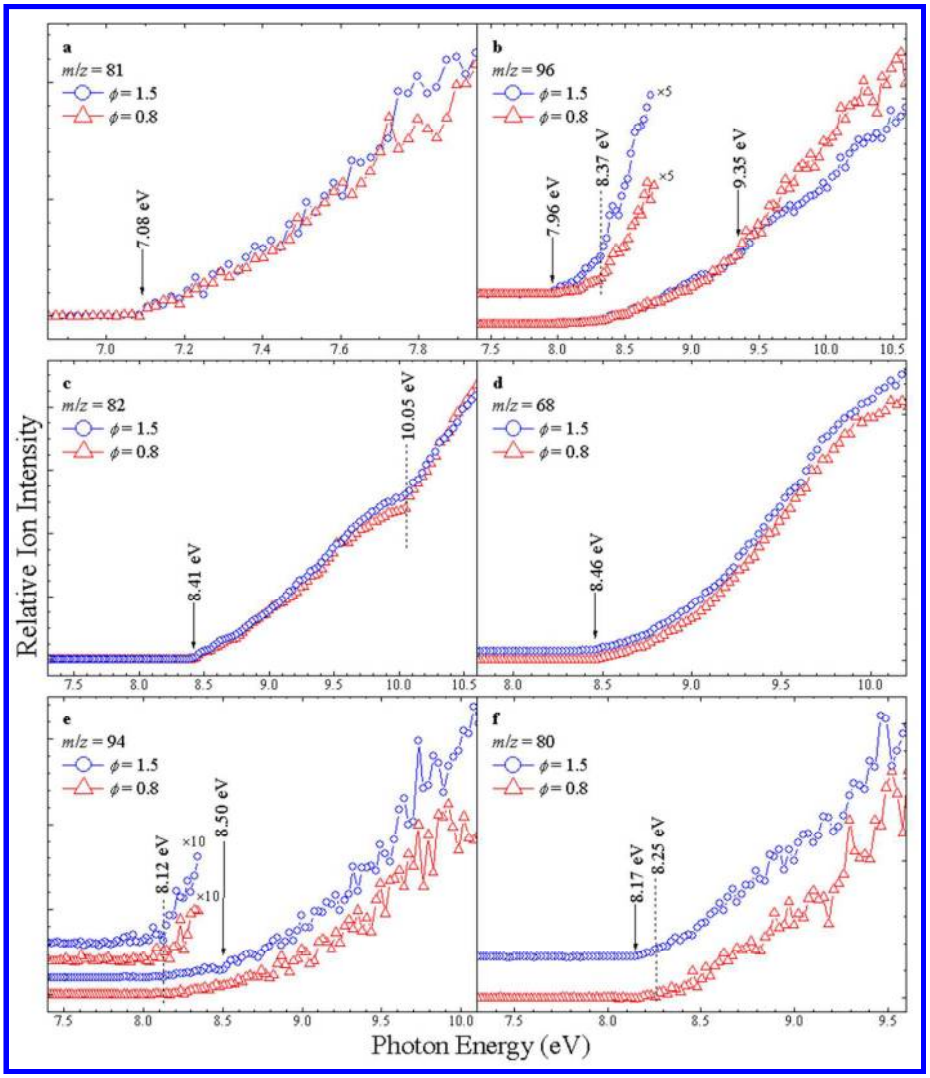


Figure 3. PIEs of the combustion intermediates in the low-pressure premixed laminar MF/O_2/Ar flames (a, *m*/*z* = 81; b, *m*/*z* = 96; c, *m*/*z* = 82; d, *m*/*z* = 68; e, *m*/*z* = 94; f, *m*/*z* = 80).

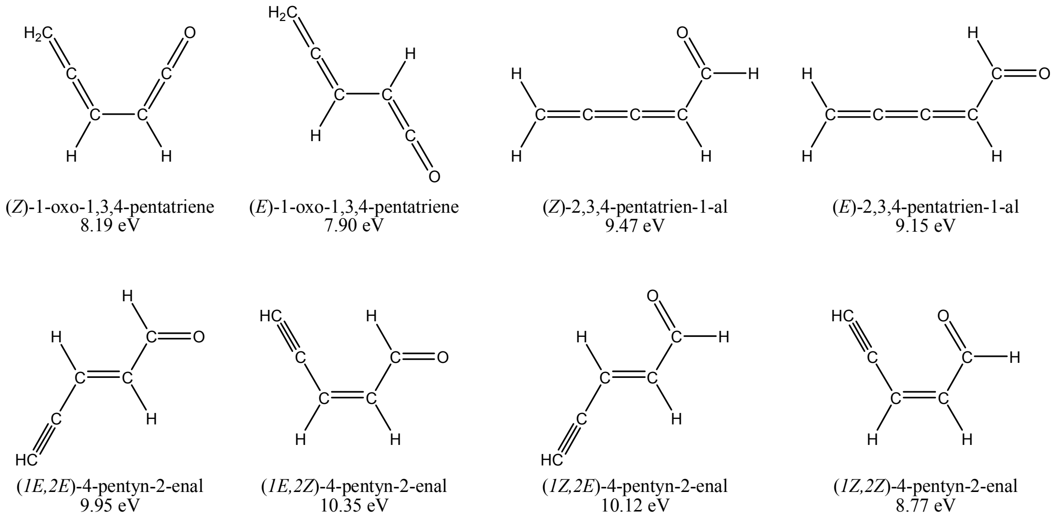


Figure 4. Structures and corresponding calculated IEs of the H-abstraction products of 3,4-pentadienaldehyde-2-yl (CH_2=C=CH–C·H–CHO).

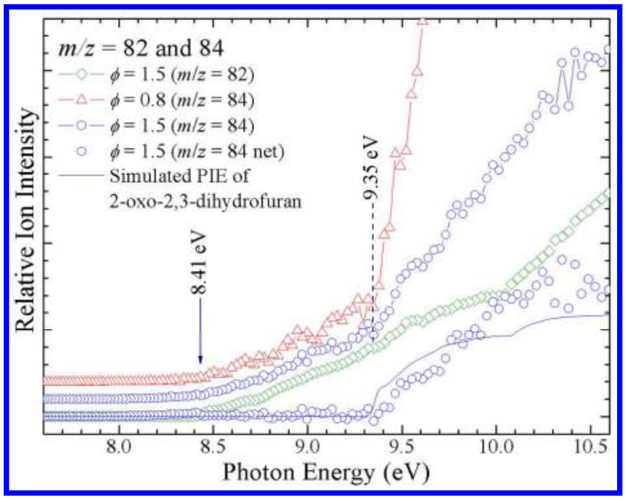


Figure 5. PIEs of the combustion intermediates of m/z = 82 and 84 in the low-pressure premixed laminar MF/O_2/Ar flames with simulated PIE of 2-oxo-2,3-dihydrofuran at B3LYP/6-311++G(2d,p) level (m/z = 84 net indicates the difference of the ion signal of m/z = 84 and that of m/z = 82, taking account into the contribution of the isotope of the fuel to this signal).

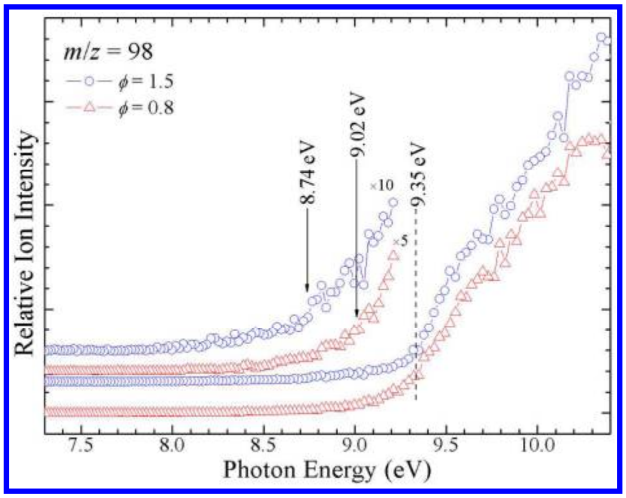


Figure 6. PIEs of the combustion intermediates of m/z = 98 in the low-pressure premixed laminar MF/O_2/Ar flames.

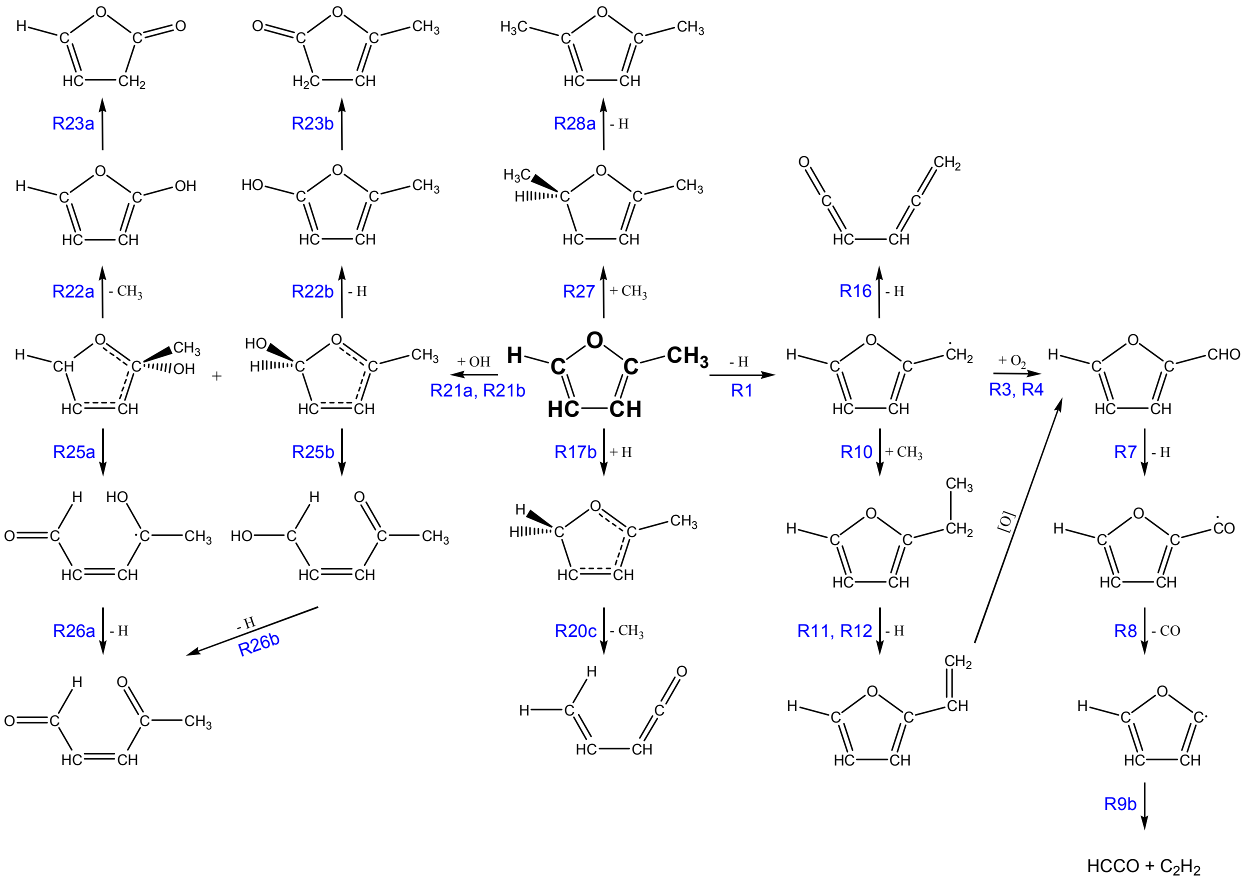


Figure 7. Primary reaction pathways of MF in flame. Labels near the arrows (Rx) correspond to the possible reactions of MF described in the text.

TABLES

Table 1. Parameters of the low-pressure premixed laminar MF/O_2/Ar flames.

Flame	MF^a ($mL\cdot min^{-1}$)	O_2 ($L\cdot min^{-1}$)	Ar ($L\cdot min^{-1}$)	Equivalence ratio
Lean	0.748	1.398	1.415	0.8
Rich	0.748	0.744	2.068	1.5

a Purchased from Shanghai Jingchun Industrial Co. Ltd.

Table 2. Primary combustion intermediates identified in the low-pressure premixed laminar MF/O_2/Ar flames.

m/*z*	Formula	IE (eV)				Combustion Intermediates
		Rich flame	Lean Flame	Literature[15]	Calculated	
64	CH_3CCCCH	9.46	---	9.50		1,3-pentadiyne
66	c-C_5H_6	8.60	8.57	8.57	8.61	cyclopentadiene
66	$CH_3CCCH{=}CH_2$	8.97	9.02	9.00		1-penten-3-yne
68	$CH_2{=}CHCH{=}C{=}O$	8.46	8.46	---	8.43; 8.45	(*E*)-1-oxo-1,3-butadiene
70	$CH_3CH_2CH{=}C{=}O$	8.80	8.82	8.80		1-oxo-1-butene
70	$CH_3CH_2CH{=}CHCH_3$	9.05	---	9.04		2-pentene
70	$CH_2{=}CHCOCH_3$	9.67	9.67	9.65		3-buten-2-one
72	$CH_3CH_2COCH_3$	9.43	9.46	9.52		2-butanone
74	C_6H_2	9.55	---	9.50		hexatriyne
76	$HCCCH{=}CHCCH$	9.05	---	9.07		3-hexa-1,5-diyne

78	C_6H_6	8.39	8.43	8.36		fulvene
78	C_6H_6	9.24	9.27	9.24378	9.30	benzene
80	CH_2=C=CH-CH=C=O	8.17	8.25	---	8.19	(*Z*)-1-oxo-1,3,4-pentatriene
81	$C_4H_3OCH_2$	7.08	7.08	---	7.05	2-furylmethyl
82	$C_4H_3OCH_3$	8.41	8.41	8.38	8.43	2-methylfuran
84	-OCHCHCH$_2$C(O)-	9.35	9.35	9.44		2-oxo-2,3-dihydrofuran
92	$C_6H_5CH_3$	8.79	8.79	8.828	8.89	toluene
94	$C_4H_3OC_2H_3$	8.12	8.12	---	8.12[11]	2-vinylfuran
94	C_6H_5OH	---	8.50	8.49		phenol
96	$CH_3C_4H_2OCH_3$	7.96	7.96	8.03		2,5-dimethylfuran
96	$C_4H_3OC_2H_5$	8.37	8.37	8.45	8.36	2-ethylfuran
96	C_4H_3OCHO	---	9.35	9.22	9.26	furfural
98	-OC(CH$_3$)CHCH$_2$C(O)-	---	9.02	---		2-oxo-2,3-dihydro-5-methylfuran
98	OHCCH=CHCOCH$_3$	9.35	9.35	---	9.33	2-penten-4-one-1-al
102	C_6H_5CCH	8.84	---	8.82		phenylacetylene
104	C_6H_5CH=CH_2	8.43	---	8.464		styrene

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Notes

The authors declare no competing financial interest.

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