# Supporting Information

# A Vacuum Ultraviolet Photoionization Study on Oxidation of JP-10 (*exo*-Tetrahydrodicyclopentadiene)

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## Data Analysis

In order to calculate the branching ratios of the products, the following relationship between the integrated ion intensity of species *i* normalized by photon flux ($S_i(T,E)$), the mole fraction ($X_i(T)$), the photoionization cross section of species *i* at a selected photon energy ($\sigma_i(E)$) and mass discrimination ($D_i$) has to be accounted for [1]:

$$S_i(T,E) \propto X_i(T) \cdot \sigma_i(E) \cdot D_i \qquad (1)$$

Equation (1) can be transformed to equations (2) and (3) expressing the relationship between the mole fraction of species *i* and *j*,

$$\frac{S_i(T,E)}{S_j(T,E)} = \frac{X_i(T)}{X_j(T)} \cdot \frac{\sigma_i(E)}{\sigma_j(E)} \cdot \frac{D_i}{D_j} \qquad (2)$$

$$\frac{X_i(T)}{X_j(T)} = \frac{S_i(T,E)}{S_j(T,E)} \cdot \frac{\sigma_j(E)}{\sigma_i(E)} \cdot \frac{D_j}{D_i} \qquad (3)$$

The branching ratios $R_i$ of the products can be then computed via equation (4):

$$R_i = \frac{X_i}{\sum X_i} \qquad (4)$$

In this work, the mass discrimination factors are determined to be $\left(\frac{x}{30}\right)^{0.36267}$ [1]. The majority of the products were quantified by exploiting photoionization cross sections at 8.0, 8.4, 9.0, 9.5, 10.0, 10.5, 11.0, and 11.5 eV. The data obtained at 14.80 eV were used to calculate the branching ratios of water ($H_2O$), carbon monoxide (CO), carbon dioxide ($CO_2$), and methane ($CH_4$). The uncertainties are 20% for experimentally measured photoionization cross sections, and a factor of 2 for the estimated [2,3].

## Discussion on potential oxidation mechanism

Based on the aforementioned findings and JP-10 pyrolysis studies within the same reactor [1], Figure S3 exhibits the proposed reaction mechanisms for the oxidation of JP-10. Note that considering the hydrocarbons, the predominant products were observed in previous JP-10 pyrolysis studies with the exception of 1,3,5-trimethylbenzene ($C_9H_{12}$), 1,2-dihydronaphthalene ($C_{10}H_{10}$), 1,4,5,8-tetrahydronaphthalene ($C_{10}H_{12}$), 2-methylpropenylbenzene ($C_{10}H_{12}$), 1-methylnaphthalene ($C_{11}H_{10}$), and biphenyl ($C_{12}H_{10}$). 1,3,5-trimethylbenzene is likely produced via hydrogen atom abstraction from toluene (P16) by a radical (atomic hydrogen, atomic oxygen, hydroxyl radical) forming 3-methylphenyl (P16-i-3) followed by methyl addition leading to *m*-xylene (P23); a second hydrogen atom abstraction from *m*-xylene followed by methyl addition to the radical center can lead to the formation of 1,3,5-trimethylbenzene (P24) [4]. However, *m*-xylene was not detected possibly due to low concentrations compared to *o*-xylene in this work. For the experimental PIE curve at *m/z* = 120, there is a little discrepancy between the onset (8.20 ± 0.05 eV) and the adiabatic ionization energy of 1,3,5-trimethylbenzene (8.40 ± 0.01 eV)[5] indicating that the $C_9H_{12}$ molecule(s) may be not attributed to 1,3,5-trimethylbenzene, but to its isomer(s) such as 1,2,3-trimethylbenzene and/or 1,2,4-trimethylbenzene. Both latter structures can be formed via molecular mass growth process from *o*-xylene (P9). Hydrogen atom abstraction from *o*-xylene at the C3 and C4 positions yields 2,3-dimethylphenyl (P9-i-2) and 3,4-dimethylphenyl (P9-i-3), which could result in the formation of 1,2,3-trimethylbenzene (P13) and 1,2,4-trimethylbenzene (P15), respectively. 1,2-Dihydronaphthalene (P35) and 1,4,5,8-tetrahydronaphthalene (P36) are proposed to be the result of multiple hydrogen atom additions to naphthalene (P34) [6]. 1-methylnaphthalene (P37) could be the product from naphthalene via hydrogen abstraction to the naphthyl radical followed by methyl addition [7]. Biphenyl (P38) is likely produced via the reaction of benzene (P26) and phenyl (P26-i) followed by hydrogen loss [8]. The process of propenyl ($C_3H_5^{\bullet}$) addition to *o*-tolyl radical (P16-i-2), which originates from a methyl loss of *o*-xylene or hydrogen atom abstraction from toluene leads eventually to 2-methylpropenylbenzene (P19). For the species already observed in pyrolysis studies [1], their formation pathways should be identical as in the present study and likely involve the decomposition routes of JP-10 disseminated earlier. Considering the relatively long residence times in the reactor, the product pool is complex. Atomic oxygen ($^{\bullet}O^{\bullet}$) and the hydroxyl radical ($OH^{\bullet}$) are produced at high concentrations, and these radicals are very reactive at elevated temperatures. This is evident from the underlying formation pathways of cyclic oxygenated species (> C5). These cyclic, oxygenated species are proposed to be produced via the oxidation processes of cyclic hydrocarbons including cyclopentadiene ($C_5H_6$), cyclopentene ($C_5H_8$), benzene ($C_6H_6$), cyclohexene ($C_6H_{10}$), and toluene ($C_7H_8$). As reported in previous pyrolysis studies [1], these cyclic species play a key role in the JP-10 decomposition processes. For cyclopentene (P31), hydrogen abstraction by atomic hydrogen, atomic oxygen, and/or the hydroxyl radical lead to the formation of cyclopentenyl radical ($C_5H_7^•$, P31-i). Sequential oxygen addition to this radical produces 2-cyclopenten-1-one ($C_5H_6O$, P32) after atomic hydrogen. Similarly, the oxidation of the cyclopentadienyl radical ($C_5H_5^•$, P33-i)), which originates from atomic hydrogen loss and/or hydrogen abstraction from cyclopentadiene (P33), produces eventually 2,4-cyclopendadiene-1-one ($C_5H_4O$, P30) [9]. Likewise, after hydrogen abstraction from cyclohexene leading to the cyclohexenyl radical ($C_6H_9^•$), oxygen addition to this radical followed by hydrogen atom loss leads to the formation of cyclohex-2-en-1-one ($C_6H_8O$). A similar process could lead to 1,4-cyclohex-2-enedione ($C_6H_6O_2$). However, cyclohex-2-en-1-one is not observed in the present work possibly due to its low concentration. It should be noticed that in our previous JP-10 pyrolysis study, the formation mechanism of cyclohexene was not located. Thus, the proposed formation pathway of 1,4-cyclohex-2-enedione is not presented in Fig. S3. The phenyl radical ($C_6H_5^•$, P26-i) is easily formed from benzene via hydrogen abstraction reactions [9]. An addition of hydroxyl to phenyl results in the formation of phenol ($C_6H_6O$, P27). Alternatively, phenol can be formed via addition of a hydroxyl radical to benzene followed by atomic hydrogen loss [10]. Further oxidation of phenol via similar pathways is likely responsible for the formation of 1,4-benzenediol ($C_6H_6O_2$, P28). The formation of *p*-benzoquinoe ($C_6H_4O_2$, P29) can be attributed to a two steps of hydrogen loss – hydrogen abstraction from 1,4-benzenediol. A decarbonylation process of 1,4-benzenediol is considered as an alternative pathway for the formation of 2,4-cyclopendadiene-1-one ($C_5H_4O$, P30) [9]. Similar to the formation of phenyl, where the oxidation process is operating at the benzoid carbon of toluene ($C_7H_8$, P16) and *o*-xylene ($C_8H_{10}$, P9), cresols ($C_7H_8O$, P20, P21, P22) and dimethylphenols ($C_8H_{10}O$) are produced, respectively. As there are three different benzoid carbon positions in toluene, three cresol isomers (orth-, meta- and para-cresols) have to be considered. For the dimethylphenol isomers, as mentioned before, it is not feasible to identify these structures due to the lack of photoionization cross sections. However, since only *o*-xylene was observed, these dimethylphenol isomers are proposed to be orth-methyl substituted, *e.g.* 2,3-dimethylphenol (P12) and 3,4-dimethylphenol (P14).

Further, the benzyl radical ($C_7H_7^•$, P16-i) – an aromatic and resonantly stabilized structure – can be easily produced from toluene via either hydrogen atom abstraction or hydrogen atom loss (decomposition). This radical plays as a key reactive intermediate for the subsequent reaction sequences. By recombination with hydroxyl, benzyl forms benzyl alcohol ($C_7H_8O$, P17). Two hydrogen atom abstractions from benzyl alcohol yield benzaldehyde ($C_7H_6O$, P18). Alternatively, by reacting with atomic oxygen followed by hydrogen atom loss, the benzyl radical is responsible for the yield of benzaldehyde. Due to the oxygen-rich condition, the second pathway for benzaldehyde is likely preferred. Similar mechanisms may apply to *o*-xylene resulting in the formation of *o*-methylbenzaldehyde ($C_8H_8O$, P11).

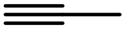
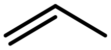
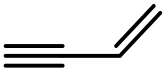
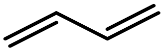
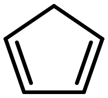
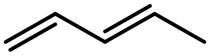
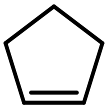
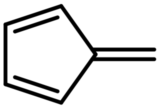
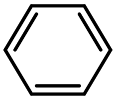
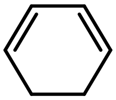
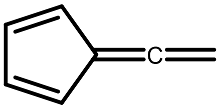
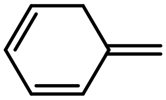
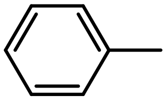
The C4 oxygenated species, 2-butenal ($C_4H_6O$), can be produced from the oxidation of 2-butene at the C4 carbon atom. Furan might be the product of a reaction of ketene with acetylene [11]. Analogously, 2,3-dihydrofuran might be produced via the reaction of ketene with ethylene. However, furan and 2,3-dihydrofuran are produced at relatively low temperatures, indicating these molecules are likely involved in the initial decomposition processes of the JP-10 oxidation. The C3 species acetone ($C_3H_6O$) and propanal ($C_3H_6O$) can be produced via the oxidation of propane ($C_3H_8$) [12]. Propane was previously observed in the pyrolysis study [1], but not detectable in the current work, possibly due to the oxygen-rich condition leading to its rapid oxidation. Ethanol ($C_2H_6O$) is likely the product from the recombination of ethyl ($C_2H_5^{\bullet}$) and hydroxyl ($OH^{\bullet}$). After two steps of hydrogen atom loss from ethanol, ethenol ($C_2H_4O$) and acetaldehyde ($C_2H_4O$) are produced. Besides, ethenol can also be produced via the reaction of atomic oxygen (O) with ethylene ($C_2H_4$). Acetaldehyde ($CH_3CHO$) can be formed via the recombination of methyl ($CH_3^{\bullet}$) with the formyl radical ($HCO^{\bullet}$) [13]. The two $C_2H_4O$ species may lose two hydrogen atoms at high temperature leading to ketene ($C_2H_2O$) [14]. Alternatively, the reaction of carbon monoxide and methylene represents an alternative formation pathway for ketene, in which methylene is formed via hydrogen loss from methyl [15].

Methanol ($CH_3OH$) is produced via the combination of a methyl radical and hydroxyl; further hydrogen loss leads to formaldehyde ($H_2CO$). Moreover, formaldehyde can also be produced via the combination of methylene radical ($CH_2$) with hydroxyl followed by atomic hydrogen loss. Formaldehyde is considered as the precursor of carbon monoxide (CO): through either hydrogen loss or abstraction reactions, formaldehyde is decomposed to the formyl radical ($HCO^{\bullet}$); a second hydrogen loss leads to carbon monoxide [14,16]. In oxygen-rich conditions and high temperatures, carbon monoxide can be easily oxidized to carbon dioxide ($CO_2$). Water ($H_2O$), as one of the terminal products, can be produced via the recombination of hydroxyl and hydrogen atom. The hydrogen abstraction reactions of JP-10 and intermediates via hydroxyl attack also contribute to the yield of water.

**Table S1.** Compilation of previous experimental studies on the pyrolysis of JP-10

| **Group** | **Method** | **Temperature (K)** | **Pressure (bar)** | **Residence time** | **Ref.** |
|---|---|---|---|---|---|
| Green et al. | Shock tube | 1000-1600 | 6-8 | 0.5 ms | [17] |
| Anderson et al. | Flow tube reactor | 298-1700 | 0.002-0.004 | 2.10-9.35 ms | [18] |
| Reyniers et al. | Flow tubular reactor | 930-1080 | 1.7 | 3.2-5.3 ms | [19] |
| Marquaire et al. | Jet-stirred reactor | 848-933 | 1 | 500-6000 ms | [20] |
| Kunzru et al. | Annular tubular reactor | 903-968 | 1 | 680-6400 ms | [21] |
| Striebich et al. | System for thermal diagnostic studies | 373-873 | 34 | 1038-5000 ms | [22] |
| Wohlwend et al. | System for thermal diagnostic studies | 473-935 | 34 | 1800 ms | [23] |
| Fang et al. | Batch reactor | 823-903 | 1-38 | 480-26400 ms | [24] |
| Fang et al. | Tubular reactor | 883-963 | 1 | $1.8\times10^6$ ms | [25] |
| Bruno et al. | Thermal block | 623-698 | 345 | $2.4\times10^5$-$7.2\times10^7$ ms | [26] |
| Kim et al. | Batch reactor | 583-683 | 40 | $3.6\times10^7$ ms | [27] |
| Liu et al. | Flow reactor | 900-1600 | 0.00667 | - | [28] |
| Kaiser et al. | Flow reactor | 1200-1600<br>949-1083 | 0.8 | tens of μs<br>124-144 ms | [1] |

**Table S2.** Compilation of products observed in our previous experiment on the decomposition of JP-10 (National Synchrotron Radiation Laboratory, NSRL).

| **Molecule** | **Formula** | **Mass** | **Structure** |
|---|---|---|---|
| $H_2$ | Hydrogen | 2 | H—H |
| $CH_4$ | Methane | 16 | $CH_4$ |
| $C_2H_2$ | Acetylene | 26 |  |
| $C_2H_4$ | Ethylene | 28 |  |
| $C_3H_4$ | Allene | 40 |  |
| $C_3H_4$ | Methylacetylene | 40 |  |
| $C_3H_6$ | Propene | 42 |  |
| $C_4H_2$ | Diacetylene | 50 |  |
| $C_4H_4$ | 1,2,3-Butatriene | 52 |  |
| $C_4H_4$ | Vinylacetylene | 52 |  |
| $C_4H_6$ | 1,3-Butadiene | 54 |  |
| $C_4H_8$ | 1-Butene | 56 |  |
| $C_4H_8$ | 2-Butene | 56 |  |
| $C_5H_6$ | Cyclopentadiene | 66 |  |
| $C_5H_8$ | 1,3-Pentadiene | 68 |  |
| $C_5H_8$ | Cyclopentene | 68 |  |
| $C_6H_6$ | Fulvene | 78 |  |
| $C_6H_6$ | Benzene | 78 |  |
| $C_6H_8$ | 1,3-Cyclohexadiene | 80 |  |
| $C_7H_6$ | Fulvenallene | 90 |  |
| $C_7H_8$ | 5-Methylene-1,3-cyclohexadiene | 92 |  |
| $C_7H_8$ | Toluene | 92 |  |

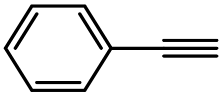
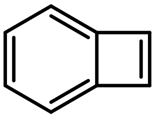
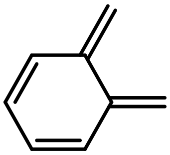
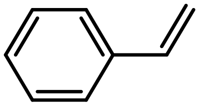
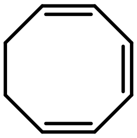
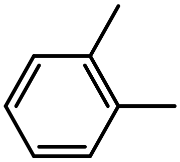
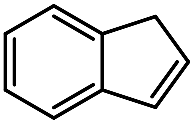
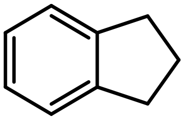
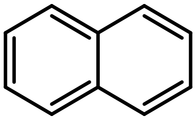
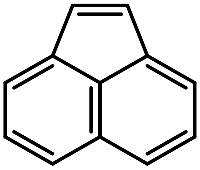
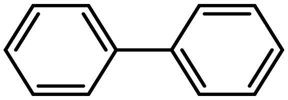
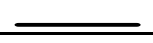
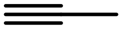
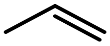
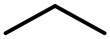
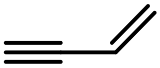
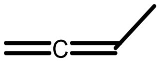
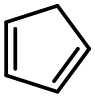
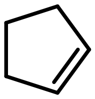
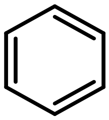
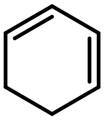
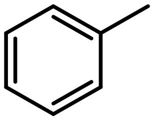
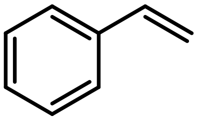
|  |  |  |  |
|---|---|---|---|
| $C_8H_6$ | Phenylacetylene | 102 |  |
| $C_8H_6$ | Benzocyclobutene | 102 |  |
| $C_8H_8$ | *o*-Xylylene | 104 |  |
| $C_8H_8$ | Styrene | 104 |  |
| $C_8H_{10}$ | 1,3,5-Cyclooctatriene | 106 |  |
| $C_8H_{10}$ | *o*-Xylene | 106 |  |
| $C_9H_8$ | Indene | 116 |  |
| $C_9H_{10}$ | Indane | 118 |  |
| $C_{10}H_8$ | Naphthalene | 128 |  |
| $C_{12}H_8$ | Acenaphthylene | 152 |  |
| $C_{12}H_{10}$ | Biphenyl | 154 |  |

**Table S3.** Compilation of previous experimental studies on the oxidation of JP-10

| **Group** | **Method** | **Temperature (K)** | **Pressure (bar)** | **Equivalence ratio** | **Residence time** | **Ref.** |
|---|---|---|---|---|---|---|
| Brophy et al. | Stationary tube system | 423 | 3.4-5.5 | 0.70-1.70 | 0-163 ms | [29] |
| Hanson et al. | Shock tube | 1200-1700 | 1.01-9.12 | 0.5, 1.0 and 2.0 | 0-1 ms | [30] |
| Seiser et al. | Counterflow flame | 1750 | 1.013 | 4.4 | - | [31] |
| Colket and Spadaccini | Shock tube | 1100-1500 | 3.04-8.11 | 0.5-1.5 | - | [32] |
| Mikolaitis et al. | Shock tube | 1200-2500 | 10.13-25.33 | 1.0 | - | [33] |
| Wang et al. | Shock tube | 1000-2100 | 1.51-5.56 | 0.25, 0.5, 1.0 and 2.0 | - | [34] |
| Green et al. | Shock tube | 1000-1600 | 6.07-8.11 | 0.14-1.0 | 0.5 ms | [17] |

**Table S4.** Species reported in previous experimental studies on JP-10 oxidation.

| **Molecule** | **Formula** | **Mass** | **Structure** | **Ref.** |
|---|---|---|---|---|
| Hydrogen | $H_2$ | 2 | $H{-}H$ | [31] |
| Methylidyne | CH | 13 | $C{-}H$ | [30,34] |
| Methane | $CH_4$ | 16 | $CH_4$ | [31] |
| Hydroxyl | OH | 17 | $^{\bullet}O{-}H$ | [30,34] |
| Acetylene | $C_2H_2$ | 26 |  | [31] |
| Carbon monoxide | CO | 28 | $^{+}O{\equiv}C^{-}$ | [31] |
| Ethylene | $C_2H_4$ | 28 |  | [17,31] |
| Ethane | $C_2H_6$ | 30 |  | [31] |
| Oxygen | O2 | 32 | $O{=}O$ | [31] |
| Carbon dioxide | CO2 | 44 | $O{=}C{=}O$ | [31] |
| Methylacetylene | $C_3H_4$ | 40 |  | [17,31] |
| Allene | $C_3H_4$ | 40 | $={C}=$ | [17,31] |
| Propene | $C_3H_6$ | 42 |  | [17,31] |
| Propane | $C_3H_8$ | 44 |  | [31] |
| Diacetylene | $C_4H_2$ | 50 |  | [17] |
| Vinylacetylene | $C_4H_4$ | 52 |  | [17] |
| 1,2-Butadiene | $C_4H_6$ | 54 |  | [17] |
| 1,3-Butadiene | $C_4H_6$ | 54 |  | [17,31] |
| 1-Butene | $C_4H_8$ | 56 |  | [17,31] |
| Cyclopentadiene | $C_5H_6$ | 66 |  | [17,31] |
| Cyclopentene | $C_5H_8$ | 68 |  | [17] |
| Benzene | $C_6H_6$ | 78 |  | [17,31] |
| 1,3-Cyclohexadiene | $C_6H_8$ | 80 |  | [17] |
| Toluene | $C_7H_8$ | 92 |  | [17] |
| Styrene | $C_8H_8$ | 104 |  | [17] |

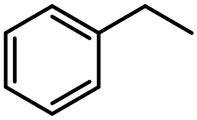
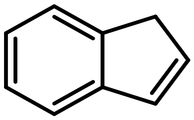
| | | | | |
|---|---|---|---|---|
| Ethylbenzene | $C_8H_{10}$ | 106 |  | [17] |
| Indene | $C_9H_8$ | 116 |  | [17] |

**Table S5.** Temperature distribution along the flow tube.

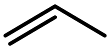
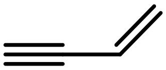
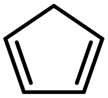
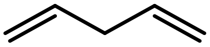
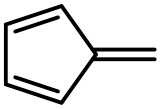
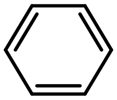
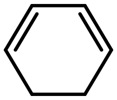
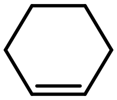
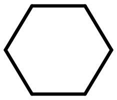
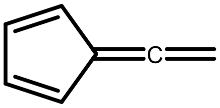
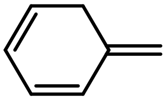
| Distance (mm) | Temperature (K) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 875 K | 900 K | 925 K | 951 K | 978 K | 1004 K | 1031 K |
| 0 | 471 | 480 | 490 | 499 | 509 | 518 | 528 |
| 10 | 541 | 556 | 571 | 586 | 601 | 616 | 632 |
| 20 | 623 | 645 | 666 | 688 | 709 | 731 | 753 |
| 30 | 694 | 719 | 745 | 770 | 796 | 821 | 847 |
| 40 | 758 | 785 | 813 | 840 | 868 | 895 | 923 |
| 50 | 791 | 820 | 849 | 877 | 906 | 935 | 964 |
| 60 | 814 | 843 | 873 | 902 | 931 | 960 | 990 |
| 70 | 830 | 859 | 888 | 916 | 945 | 974 | 1003 |
| 80 | 843 | 871 | 900 | 928 | 957 | 985 | 1014 |
| 90 | 852 | 880 | 908 | 936 | 964 | 992 | 1020 |
| 100 | 856 | 884 | 912 | 940 | 968 | 996 | 1024 |
| 110 | 862 | 890 | 917 | 945 | 972 | 1000 | 1028 |
| 120 | 866 | 893 | 921 | 948 | 975 | 1003 | 1030 |
| 130 | 869 | 896 | 923 | 950 | 976 | 1003 | 1030 |
| 140 | 872 | 898 | 925 | 951 | 978 | 1004 | 1031 |
| 150 | 872 | 898 | 924 | 950 | 976 | 1002 | 1029 |
| 160 | 874 | 900 | 925 | 951 | 977 | 1002 | 1028 |
| 170 | 875 | 900 | 925 | 950 | 975 | 1000 | 1025 |
| 180 | 875 | 899 | 924 | 948 | 973 | 997 | 1022 |
| 190 | 873 | 897 | 921 | 945 | 968 | 992 | 1016 |
| 200 | 870 | 893 | 916 | 939 | 961 | 984 | 1007 |
| 210 | 857 | 878 | 900 | 921 | 942 | 964 | 985 |
| 220 | 829 | 848 | 866 | 885 | 904 | 922 | 941 |

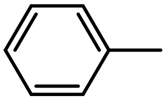
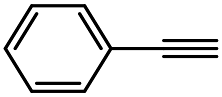
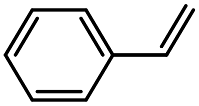
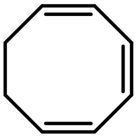
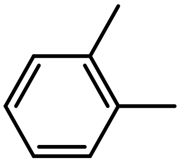
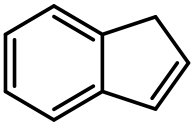
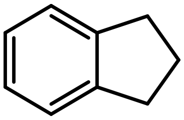
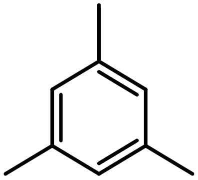
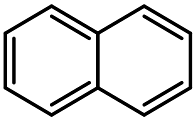
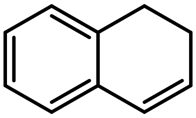
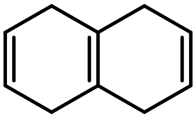
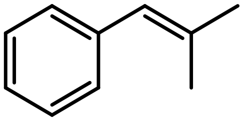
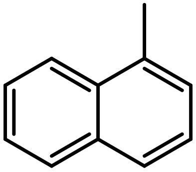
**Table S6.** Photoionization cross sections (Mb, 1 Mb = $10^{-22}$ $m^2$) of the products at selected energies exploited for the calculations of the branching ratios in this work.

| Species | Formula | Mass | Reference IE (eV) | Photon Energy (eV) | | | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 8.0 | 8.4 | 9.0 | 9.5 | 10.0 | 10.5 | 11.0 | 11.5 | 14.8 | |
| Methane | $CH_4$ | 16 | 12.61 | - | - | - | - | - | - | - | - | 25.65 | [35] |
| Water | $H_2O$ | 18 | 12.62 | - | - | - | - | - | - | - | - | 12.64 | [36] |
| Acetylene | $C_2H_2$ | 26 | 11.40 | - | - | - | - | - | - | - | 18.26 | - | [3] |
| Carbon monoxide | $CO$ | 28 | 14.00 | - | - | - | - | - | - | - | - | 22.56 | [37] |
| Ethylene | $C_2H_4$ | 28 | 10.51 | - | - | - | - | - | 0.92 | 7.79 | 8.02 | - | [35] |
| Formaldehyde | $CH_2O$ | 30 | 10.88 | - | - | - | - | - | - | 13.65 | 18.26 | - | Est. |
| Methanol | $CH_4O$ | 32 | 10.84 | - | - | - | - | - | - | 3.33 | 9.404 | - | [5] |
| Allene | $C_3H_4$ | 40 | 9.69 | - | - | - | - | 5.66 | 15.48 | 22.26 | 25.84 | - | [38] |
| Methylacetylene | $C_3H_4$ | 40 | 10.36 | - | - | - | - | - | 23.06 | 43.84 | 42.1 | - | [35] |
| Ketene | $C_2H_2O$ | 42 | 9.62 | - | - | - | - | 21.26 | 24.83 | 15.81 | 13.01 | - | [38] |
| Propene | $C_3H_6$ | 42 | 9.73 | - | - | - | - | 7.05 | 11.09 | 12.41 | 13.35 | - | [39] |
| Ethenol | $C_2H_4O$ | 44 | 9.33 | - | - | - | 1.68 | 6.38 | 9.72 | - | - | - | [39] |
| Acetaldehyde | $C_2H_4O$ | 44 | 10.23 | - | - | - | - | 0.02 | 7.44 | 7.96 | 9.28 | - | [39] |
| Carbon dioxide | $CO_2$ | 44 | 13.78 | - | - | - | - | - | - | - | - | 15.50 | [40] |
| Ethanol | $C_2H_6O$ | 46 | 10.48 | - | - | - | - | - | 0.62 | 4.88 | 5.24 | - | [3] |
| 1,2,3-butatriene | $C_4H_4$ | 52 | 9.25 | - | - | 0.02 | 3.89 | 7.54 | 8.43 | 10.29 | 12.14 | - | Est. |
| Vinylacetylene | $C_4H_4$ | 52 | 9.58 | - | - | - | 0.25 | 24.49 | 33.83 | 37.61 | 39.92 | - | [3] |
| 1,3-Butadiene | $C_4H_6$ | 54 | 9.07 | - | - | 0.02 | 8.48 | 13.96 | 16.44 | 19.91 | 22.45 | - | [38] |
| 1-Butene | $C_4H_8$ | 56 | 9.55 | - | - | - | 0 | 9.43 | 9.91 | 11.1 | 12.42 | - | [41] |
| *cis*-2-Butene | $C_4H_8$ | 56 | 9.11 | - | - | 0.01 | 5.24 | 9.06 | 11.04 | 14.05 | 19.17 | - | [41] |
| Propanal | $C_3H_6O$ | 58 | 9.96 | - | - | - | - | 1.91 | 9.59 | 10.77 | 11.33 | - | [41] |
| Acetone | $C_3H_6O$ | 58 | 9.70 | - | - | - | 0 | 7.71 | 11.36 | 10.12 | 9.63 | - | [5] |
| Cyclopentadiene | $C_5H_6$ | 66 | 8.57 | - | - | 8.52 | 10.05 | - | - | - | - | - | [42] |
| Furan | $C_4H_4O$ | 68 | 8.88 | - | - | 1.93 | 7.89 | 11.14 | 14.40 | 18.28 | 20.99 | - | [38] |
| 1,4-Pentadiene | $C_5H_8$ | 68 | 9.62 | - | - | - | 0.31 | 13.40 | 18.44 | 18.41 | 17.82 | - | [38] |
| 2-Butenal | $C_4H_6O$ | 70 | 9.75 | - | - | - | - | 3.88 | 11.21 | 14.01 | 15.30 | - | [38] |
| 2,3-Dihydrofuran | $C_4H_6O$ | 70 | 8.33 | - | 0.51 | 5.78 | 9.24 | 11.60 | 11.31 | 11.80 | 10.97 | - | [38] |
| Fulvene | $C_6H_6$ | 78 | 8.36 | - | 1.37 | 39.55 | 41.89 | 41.89 | 41.89 | - | - | - | [43] |
| Benzene | $C_6H_6$ | 78 | 9.24 | - | - | - | 11.05 | 24.28 | 31.81 | 38.60 | 39.25 | - | [3] |
| 1,3-Cyclohexadiene | $C_6H_8$ | 80 | 8.25 | - | 7.67 | 20.32 | 18.39 | 22.52 | 27.65 | 35.76 | 37.3 | - | [41] |
| 2,4-Cyclopentadiene-1-one | $C_5H_4O$ | 80 | 9.42 | - | - | - | 1.58 | 13.69 | 24.01 | 31.02 | - | - | Est. |
| Cyclohexene | $C_6H_{10}$ | 82 | 8.95 | - | - | 1.5 | 8.90 | 11.56 | 14.81 | 18.02 | 19.46 | - | [41] |
| 2-Cyclopenten-1-one | $C_5H_6O$ | 82 | 9.38 | - | - | - | 3.65 | 10.85 | 21.87 | - | - | - | Est. |
| 2,4-Hexadiene | $C_6H_{10}$ | 82 | 8.19 | 0 | 5.46 | 17.91 | 21.34 | 22.10 | 18.25 | 16.43 | - | - | Est. |
| 1-Hexene | $C_6H_{12}$ | 84 | 9.44 | - | - | - | 0.89 | 8.58 | 9.65 | 8.86 | 9.00 | - | [38] |
| *trans*-2-Hexene | $C_6H_{12}$ | 84 | 8.97 | - | - | 0.93 | 8.14 | 12.88 | 12.20 | 12.481 | 12.21 | - | [38] |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cyclohexane | $C_6H_{12}$ | 84 | 9.88 | - | - | - | - | 1.57 | 20.27 | 43.39 | 45.28 | - | [5] |
| Fulvenallene | $C_7H_6$ | 90 | 8.29 | - | 1.88 | 11.73 | 18.25 | 22.11 | 30.00 | 33.31 | 31.12 | - | Est. |
| 5-Methylene-1,3-cyclohexadiene | $C_7H_8$ | 92 | 7.90 | 0.72 | 2.99 | 4.53 | 7.85 | 8.94 | 14.01 | - | - | - | Est. |
| Toluene | $C_7H_8$ | 92 | 8.83 | - | - | 5.02 | 18.54 | 26.02 | 31.29 | 39.33 | 51.27 | - | [5] |
| Phenol | $C_6H_6O$ | 94 | 8.94 | - | 0 | 12.88 | 24.10 | 34.02 | - | - | - | - | [42] |
| Phenylacetylene | $C_8H_6$ | 102 | 8.82 | - | - | 14.82 | 29.39 | 52.4 | 62.42 | 76.97 | 101.21 | - | [5] |
| Styrene | $C_8H_8$ | 104 | 8.46 | - | 0.01 | 10.36 | 26.33 | 32.08 | 43.19 | 56.81 | 66.9 | - | [5] |
| 1,3,5-Cyclooctatriene | $C_8H_{10}$ | 106 | 7.90 | 3.24 | 10.07 | 13.16 | 16.48 | 18.77 | - | - | - | - | Est. |
| *o*-Xylene | $C_8H_{10}$ | 106 | 8.56 | - | - | 8.22 | 17.68 | 24.17 | 34.08 | 45.44 | 53.04 | - | [5] |
| Benzaldehyde | $C_7H_6O$ | 106 | 9.50 | - | - | - | 0.28 | 21.88 | 36.32 | 39.84 | 47.96 | - | [5] |
| *p*-Benzoquinone | $C_6H_4O_2$ | 108 | 10.00 | - | - | - | - | 0.14 | 33.33 | 49.60 | - | - | Est. |
| Cresols | $C_7H_8O$ | 108 | 8.30 | - | 1.29 | 17.74 | 25.47 | 27.54 | 27.86 | 29.09 | - | - | Est. |
| Benzyl alcohol | $C_7H_8O$ | 108 | 8.85 | - | - | 0.86 | 14.21 | 23.74 | 28.20 | 28.16 | 29.06 | - | [5] |
| 1,4-Cyclohex-2-enedione | $C_6H_6O_2$ | 110 | 9.77 | - | - | - | - | 3.68 | 29.81 | 46.46 | - | - | Est. |
| 1,4-Benzenediol | $C_6H_6O_2$ | 110 | 7.95 | 0.2 | 0.9 | 9.74 | 20.04 | 35.00 | 35.00 | 35.00 | - | - | Est. |
| Indene | $C_9H_8$ | 116 | 8.14 | - | 3.37 | 13.60 | 27.61 | 40.58 | 52.19 | 62.87 | 86.32 | - | [5] |
| Indane | $C_9H_{10}$ | 118 | 8.54 | - | 0.01 | 8.36 | 18.70 | 26.70 | 33.29 | 42.75 | 57.60 | - | [5] |
| Methylbenzaldehydes | $C_8H_8O$ | 120 | 9.33 | - | - | - | 4.79 | 31.03 | 42.77 | 48.02 | 55.47 | - | Est. |
| 1,3,5-Trimethylbenzene | $C_9H_{12}$ | 120 | 8.40 | - | 0.21 | 12.90 | 21.37 | 29.46 | 38.82 | 52.24 | 64.59 | - | [5] |
| Dimethylphenols | $C_8H_{10}O$ | 122 | 8.10 | - | 5.80 | 24.66 | 53.59 | 74.44 | 108.03 | - | - | - | Est. |
| Naphthalene | $C_{10}H_8$ | 128 | 8.14 | - | 4.49 | 13.22 | 21.34 | 39.81 | 51.74 | 61.42 | 86.99 | - | Est. |
| 1,2-Dihydronaphthalene | $C_{10}H_{10}$ | 130 | 8.00 | 0.21 | 5.64 | 15.46 | 28.83 | 40.71 | 51.75 | 65.84 | 90.99 | - | Est. |
| 1,4,5,8-Tetrahydronaphthalene | $C_{10}H_{12}$ | 132 | 8.46 | - | - | 7.71 | 15.37 | 23.20 | 29.21 | 35.02 | 41.22 | - | Est. |
| 2-Methylpropenylbenzene | $C_{10}H_{12}$ | 132 | 7.78 | 7.17 | 19.32 | 30.23 | 36.31 | 45.79 | 60.21 | - | - | - | Est. |
| 1-Methylnaphthalene | $C_{11}H_{10}$ | 142 | 7.96 | 1.77 | 6.67 | 13.98 | 21.80 | 39.97 | 53.47 | 66.23 | 92.35 | - | [5] |
| Biphenyl | $C_{12}H_{10}$ | 154 | 8.16 | - | 2.53 | 9.14 | 21.22 | 34.51 | 50.62 | 58.65 | - | - | Est. |

**Table S7.** Compilation of hydrocarbons observed in the oxidation of JP-10.

| **Species** | **Formula** | **Mass** | **Structure** |
|---|---|---|---|
| Methane | $CH_4$ | 16 | $CH_4$ |
| Acetylene | $C_2H_2$ | 26 |  |
| Ethylene | $C_2H_4$ | 28 |  |
| Allene | $C_3H_4$ | 40 |  |
| Methylacetylene | $C_3H_4$ | 40 |  |
| Propene | $C_3H_6$ | 42 |  |
| 1,2,3-butatriene | $C_4H_4$ | 52 |  |
| Vinylacetylene | $C_4H_4$ | 52 |  |
| 1,3-Butadiene | $C_4H_6$ | 54 |  |
| 1-Butene | $C_4H_8$ | 56 |  |
| *cis*-2-Butene | $C_4H_8$ | 56 |  |
| Cyclopentadiene | $C_5H_6$ | 66 |  |
| 1,4-Pentadiene | $C_5H_8$ | 68 |  |
| Fulvene | $C_6H_6$ | 78 |  |
| Benzene | $C_6H_6$ | 78 |  |
| 1,3-Cyclohexadiene | $C_6H_8$ | 80 |  |
| Cyclohexene | $C_6H_{10}$ | 82 |  |
| 2,4-Hexadiene | $C_6H_{10}$ | 82 |  |
| 1-Hexene | $C_6H_{12}$ | 84 |  |
| trans-2-Hexene | $C_6H_{12}$ | 84 |  |
| Cyclohexane | $C_6H_{12}$ | 84 |  |
| Fulvenallene | $C_7H_6$ | 90 |  |
| 5-Methylene-1,3-cyclohexadiene | $C_7H_8$ | 92 |  |

| | | | |
|---|---|---|---|
| Toluene | $C_7H_8$ | 92 |  |
| Phenylacetylene | $C_8H_6$ | 102 |  |
| Styrene | $C_8H_8$ | 104 |  |
| 1,3,5-Cyclooctatriene | $C_8H_{10}$ | 106 |  |
| *o*-Xylene | $C_8H_{10}$ | 106 |  |
| Indene | $C_9H_8$ | 116 |  |
| Indane | $C_9H_{10}$ | 118 |  |
| 1,3,5-Trimethylbenzene | $C_9H_{12}$ | 120 |  |
| Naphthalene | $C_{10}H_8$ | 128 |  |
| 1,2-Dihydronaphthalene | $C_{10}H_{10}$ | 130 |  |
| 1,4,5,8-Tetrahydronaphthalene | $C_{10}H_{12}$ | 132 |  |
| 2-Methylpropenylbenzene | $C_{10}H_{12}$ | 132 |  |
| 1-Methylnaphthalene | $C_{11}H_{10}$ | 142 |  |

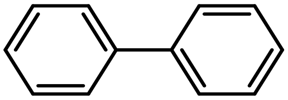
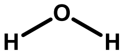
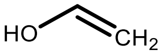
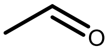
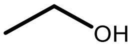
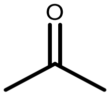
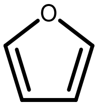
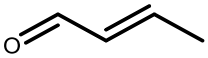
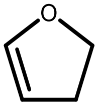
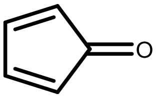
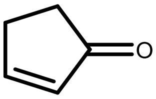
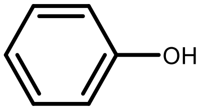
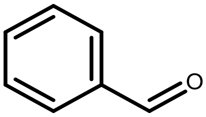
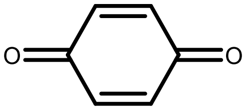
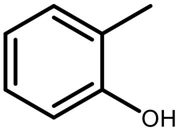
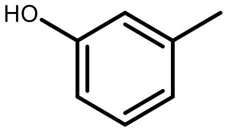
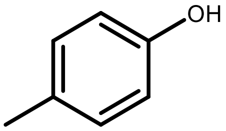
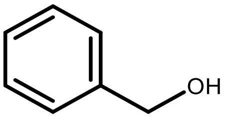
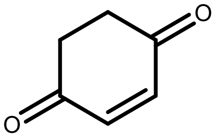
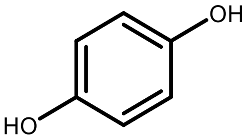
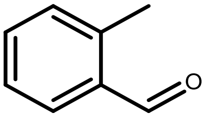
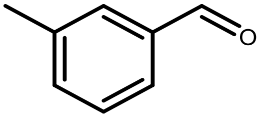
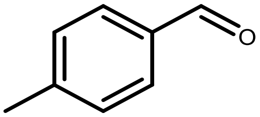
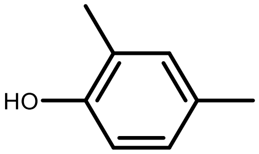
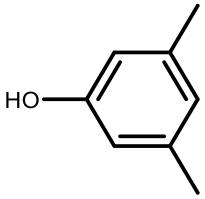
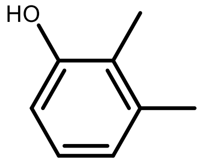
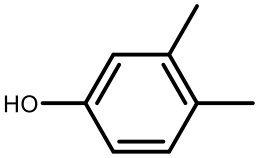
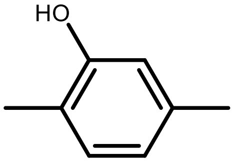
| | | | |
|---|---|---|---|
| Biphenyl | $C_{12}H_{10}$ | 154 |  |

**Table S8.** Compilation of oxygenated species observed in the oxidation of JP-10.

| Species | Formula | Mass | Structure |
|---|---|---|---|
| Water | $H_2O$ | 18 |  |
| Carbon monoxide | CO | 28 | $^{+}O{\equiv}C^{-}$ |
| Formaldehyde | $CH_2O$ | 30 | $H_2C{=}O$ |
| Methanol | $CH_4O$ | 32 | $H_3C{-}OH$ |
| Ketene | $C_2H_2O$ | 42 | $O{=}C{=}CH_2$ |
| Ethenol | $C_2H_4O$ | 44 |  |
| Acetaldehyde | $C_2H_4O$ | 44 |  |
| Carbon dioxide | $CO_2$ | 44 | $O{=}C{=}O$ |
| Ethanol | $C_2H_6O$ | 46 |  |
| Propanal | $C_3H_6O$ | 58 |  |
| Acetone | $C_3H_6O$ | 58 |  |
| Furan | $C_4H_4O$ | 68 |  |
| 2-Butenal | $C_4H_6O$ | 70 |  |
| 2,3-Dihydrofuran | $C_4H_6O$ | 70 |  |
| 2,4-Cyclopentadiene-1-one | $C_5H_4O$ | 80 |  |
| 2-Cyclopenten-1-one | $C_5H_6O$ | 82 |  |
| Phenol | $C_6H_6O$ | 94 |  |
| Benzaldehyde | $C_7H_6O$ | 106 |  |
| *p*-Benzoquinone | $C_6H_4O_2$ | 108 |  |
| Cresols | $C_7H_8O$ | 108 |  ,  ,  |

| | | | |
|---|---|---|---|
| Benzyl alcohol | $C_7H_8O$ | 108 |  |
| 1,4-Cyclohex-2-enedione | $C_6H_6O_2$ | 110 |  |
| 1,4-Benzenediol | $C_6H_6O_2$ | 110 |  |
| Methylbenzaldehydes | $C_8H_8O$ | 120 |  ,  ,  |
| Dimethylphenols | $C_{10}H_{10}O$ | 122 |  ,  ,  , <br>  ,  |

**Note:** Due to the lack of precise photoionization cross sections and/or PIE curves, some species cannot be identified and merged into classes including Cresols, Methylbenzaldehydes and Dimethylphenols.

**Table S9.** Mole fractions of the products in the oxidation of JP-10 at 600 Torr in the chemical reactor at 925, 951, 978, 1004 and 1031 K. The numbers in each bracket present the lower and upper uncertainties, respectively. Some of the error bars are quite large due to the relatively high uncertainties of photoionization cross sections (20% for experimentally measured photoionization cross sections, and a factor of 2 for the estimated).

| Molecules | Formula | Temperature | | | | |
|---|---|---|---|---|---|---|
| | | 925 K | 951 K | 978 K | 1004 K | 1031 K |
| Methane | $CH_4$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 7.214E-06 (-1.082E-06, 1.082E-06) | 6.734E-06 (-1.010E-06, 1.010E-06) |
| Water | $H_2O$ | 6.509E-05 (-9.763E-06, 9.763E-06) | 7.575E-05 (-1.136E-05, 1.136E-05) | 1.167E-04 (-1.750E-05, 1.750E-05) | 5.137E-04 (-7.705E-05, 7.705E-05) | 1.037E-03 (-1.555E-04, 1.555E-04) |
| Acetylene | $C_2H_2$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 1.548E-05 (-4.997E-06, 4.997E-06) | 1.241E-05 (-6.060E-06, 6.060E-06) |
| Carbon monoxide | $CO$ | 8.839E-06 (-1.326E-06, 1.326E-06) | 1.511E-05 (-2.266E-06, 2.266E-06) | 1.700E-04 (-2.550E-05, 2.550E-05) | 9.780E-04 (-1.467E-04, 1.467E-04) | 1.548E-03 (-2.322E-04, 2.322E-04) |
| Ethylene | $C_2H_4$ | 0 (0, 0) | 0 (0, 0) | 2.900E-05 (-1.144E-05, 1.144E-05) | 7.499E-05 (-2.605E-05, 2.605E-05) | 1.413E-05 (-5.815E-06, 5.815E-06) |
| Formaldehyde | $CH_2O$ | 4.273E-07 (-2.841E-07, 4.978E-07) | 1.175E-06 (-8.176E-07, 1.405E-06) | 8.002E-06 (-6.569E-06, 1.057E-05) | 2.649E-05 (-1.832E-05, 3.157E-05) | 7.009E-06 (-5.203E-06, 8.708E-06) |
| Methanol | $CH_4O$ | 0 (0, 0) | 0 (0, 0) | 2.213E-07 (-1.409E-07, 1.409E-07) | 9.207E-07 (-4.501E-07, 4.501E-07) | 6.944E-07 (-1.874E-07, 1.874E-07) |
| Allene | $C_3H_4$ | 0 (0, 0) | 0 (0, 0) | 8.276E-07 (-1.571E-07, 1.571E-07) | 4.196E-06 (-1.142E-06, 1.142E-06) | 5.861E-07 (-3.309E-07, 3.309E-07) |
| Methylacetylene | $C_3H_4$ | 0 (0, 0) | 0 (0, 0) | 6.709E-07 (-2.228E-07, 2.228E-07) | 3.928E-06 (-1.177E-06, 1.177E-06) | 5.439E-07 (-1.599E-07, 1.599E-07) |
| Ketene | $C_2H_2O$ | 0 (0, 0) | 0 (0, 0) | 3.026E-06 (-3.480E-06, 3.480E-06) | 2.219E-05 (-1.286E-05, 1.286E-05) | 1.109E-06 (-1.275E-06, 1.275E-06) |
| Propene | $C_3H_6$ | 4.490E-07 | 7.204E-07 | 4.259E-06 | 1.104E-05 | 1.429E-06 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  | (-2.488E-07, 2.488E-07) | (-8.285E-07, 8.285E-07) | (-4.829E-06, 4.829E-06) | (-9.113E-06, 9.113E-06) | (-1.643E-06, 1.643E-06) |
| Ethenol | $C_2H_4O$ | 0 (0, 0) | 0 (0, 0) | 2.546E-07 (-2.928E-07, 2.928E-07) | 1.263E-06 (-1.926E-07, 1.926E-07) | 2.821E-07 (-1.797E-07, 1.797E-07) |
| Acetaldehyde | $C_2H_4O$ | 0 (0, 0) | 0 (0, 0) | 1.887E-06 (-3.192E-07, 3.192E-07) | 1.602E-05 (-2.948E-06, 2.948E-06) | 1.214E-06 (-3.809E-07, 3.809E-07) |
| Carbon dioxide | $CO_2$ | 6.486E-06 (-9.729E-07, 9.729E-07) | 2.123E-05 (-3.185E-06, 3.185E-06) | 3.317E-05 (-4.976E-06, 4.976E-06) | 1.677E-04 (-2.516E-05, 2.516E-05) | 8.605E-04 (-1.291E-04, 1.291E-04) |
| Ethanol | $C_2H_6O$ | 0 (0, 0) | 0 (0, 0) | 1.352E-05 (-2.754E-06, 2.754E-06) | 1.005E-05 (-3.961E-06, 3.961E-06) | 1.226E-05 (-4.637E-06, 4.637E-06) |
| 1,2,3-butatriene | $C_4H_4$ | 0 (0, 0) | 0 (0, 0) | 2.018E-07 (-3.028E-07, 4.037E-07) | 1.344E-07 (-2.016E-07, 2.688E-07) | 0 (0, 0) |
| Vinylacetylene | $C_4H_4$ | 0 (0, 0) | 0 (0, 0) | 1.114E-07 (-1.005E-07, 1.005E-07) | 2.607E-06 (-5.979E-07, 5.979E-07) | 3.646E-07 (-2.078E-07, 2.078E-07) |
| 1,3-Butadiene | $C_4H_6$ | 0 (0, 0) | 0 (0, 0) | 7.686E-06 (-2.067E-06, 2.067E-06) | 3.506E-05 (-7.603E-06, 7.603E-06) | 4.075E-07 (-2.278E-07, 2.278E-07) |
| 1-Butene | $C_4H_8$ | 0 (0, 0) | 3.724E-07 (-3.278E-07, 3.278E-07) | 1.326E-05 (-8.062E-06, 8.062E-06) | 3.560E-05 (-1.206E-05, 1.206E-05) | 1.723E-06 (-3.854E-07, 3.854E-07) |
| cis-2-Butene | $C_4H_8$ | 0 (0, 0) | 1.316E-07 (-1.514E-07, 1.514E-07) | 1.098E-06 (-5.660E-07, 5.660E-07) | 9.477E-06 (-5.114E-06, 5.114E-06) | 3.023E-07 (-3.477E-07, 3.477E-07) |
| Propanal | $C_3H_6O$ | 0 (0, 0) | 0 (0, 0) | 7.415E-06 (-1.808E-06, 1.808E-06) | 8.578E-06 (-2.492E-06, 2.492E-06) | 6.274E-06 (-1.051E-06, 1.051E-06) |
| Acetone | $C_3H_6O$ | 0 (0, 0) | 0 (0, 0) | 9.761E-06 (-3.323E-06, 3.323E-06) | 1.010E-05 (-3.426E-06, 3.426E-06) | 9.495E-06 (-2.585E-06, 2.585E-06) |
| Cyclopentadiene | $C_5H_6$ | 1.440E-06 (-5.312E-07, 5.312E-07) | 9.628E-06 (-2.955E-06, 2.955E-06) | 9.381E-05 (-2.171E-05, 2.171E-05) | 9.900E-05 (-3.692E-05, 3.692E-05) | 3.578E-07 (-3.354E-07, 3.354E-07) |
| Furan | $C_4H_4O$ | 9.455E-07 | 6.189E-06 | 4.010E-05 | 2.465E-05 | 9.619E-07 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | (-3.559E-07, 3.559E-07) | (-2.197E-06, 2.197E-06) | (-1.663E-05, 1.663E-05) | (-9.939E-06, 9.939E-06) | (-7.671E-07, 7.671E-07) |
| 1,4-Pentadiene | $C_5H_8$ | 1.905E-06 (-4.246E-07, 4.246E-07) | 3.787E-06 (-7.043E-07, 7.043E-07) | 3.016E-05 (-4.684E-06, 4.684E-06) | 1.308E-05 (-3.978E-06, 3.978E-06) | 3.572E-07 (-7.783E-08, 7.783E-08) |
| 2-Butenal | $C_4H_6O$ | 0 (0, 0) | 0 (0, 0) | 3.099E-06 (-6.449E-07, 6.449E-07) | 9.862E-06 (-2.509E-06, 2.509E-06) | 7.236E-07 (-2.422E-07, 2.422E-07) |
| 2,3-Dihydrofuran | $C_4H_6O$ | 0 (0, 0) | 0 (0, 0) | 6.442E-07 (-3.656E-07, 3.656E-07) | 1.166E-06 (-3.910E-07, 3.910E-07) | 4.844E-08 (-5.571E-08, 5.571E-08) |
| Fulvene | $C_6H_6$ | 6.110E-07 (-2.007E-07, 2.007E-07) | 3.847E-06 (-2.635E-06, 2.635E-06) | 2.862E-05 (-4.799E-06, 4.799E-06) | 9.812E-06 (-2.107E-06, 2.107E-06) | 0 (0, 0) |
| Benzene | $C_6H_6$ | 0 (0, 0) | 2.559E-07 (-2.942E-07, 2.942E-07) | 2.752E-06 (-1.534E-06, 1.534E-06) | 4.461E-05 (-8.141E-06, 8.141E-06) | 1.191E-05 (-2.763E-06, 2.763E-06) |
| 1,3-Cyclohexadiene | $C_6H_8$ | 0 (0, 0) | 3.148E-07 (-2.110E-07, 2.110E-07) | 5.951E-06 (-1.688E-06, 1.688E-06) | 7.576E-06 (-1.698E-06, 1.698E-06) | 5.775E-08 (-6.642E-08, 6.642E-08) |
| 2,4-Cyclopentadiene-1-one | $C_5H_4O$ | 2.608E-08 (-3.912E-08, 5.216E-08) | 1.373E-07 (-1.084E-07, 1.771E-07) | 2.275E-06 (-1.169E-06, 2.307E-06) | 3.895E-06 (-2.693E-06, 4.641E-06) | 3.868E-08 (-3.768E-08, 5.702E-08) |
| Cyclohexene | $C_6H_{10}$ | 1.232E-05 (-1.417E-05, 1.417E-05) | 4.819E-05 (-4.394E-05, 4.394E-05) | 7.476E-04 (-1.184E-04, 1.184E-04) | 1.125E-03 (-1.973E-04, 1.973E-04) | 0 (0, 0) |
| 2-Cyclopenten-1-one | $C_5H_6O$ | 1.822E-07 (-2.733E-07, 3.644E-07) | 1.068E-06 (-8.407E-07, 1.375E-06) | 1.558E-05 (-8.780E-06, 1.657E-05) | 3.068E-05 (-1.856E-05, 3.390E-05) | 5.988E-07 (-3.596E-07, 6.590E-07) |
| 2,4-Hexadiene | $C_6H_{12}$ | 0 (0, 0) | 0 (0, 0) | 1.118E-05 (-1.676E-06, 1.676E-06) | 1.801E-05 (-2.702E-06, 2.702E-06) | 6.141E-07 (-9.211E-08, 9.211E-08) |
| 1-Hexene | $C_6H_{12}$ | 0 (0, 0) | 2.600E-07 (-4.855E-08, 4.855E-08) | 1.134E-07 (-1.304E-07, 1.304E-07) | 2.330E-07 (-2.679E-07, 2.679E-07) | 0 (0, 0) |
| trans-2-Hexene | $C_6H_{12}$ | 0 (0, 0) | 9.558E-07 (-5.456E-07, 5.456E-07) | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) |
| Cyclohexane | $C_6H_{12}$ | 0 (0, 0) | 3.291E-07 | 9.700E-07 | 2.684E-07 | 1.935E-08 |

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| | | | (-2.101E-07, 3.746E-07) | (-1.455E-06, 1.940E-06) | (-4.026E-07, 5.367E-07) | (-2.903E-08, 3.871E-08) |
| Fulvenallene | $C_7H_6$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 1.676E-09 (-9.307E-10, 1.769E-09) | 0 (0, 0) |
| 5-Methylene-1,3-cyclohexadiene | $C_7H_8$ | 2.627E-06 (-8.228E-07, 8.228E-07) | 1.860E-05 (-7.900E-06, 7.900E-06) | 1.091E-04 (-3.393E-05, 3.393E-05) | 6.879E-05 (-1.763E-05, 1.763E-05) | 0 (0, 0) |
| Toluene | $C_7H_8$ | 4.012E-07 (-1.399E-07, 1.399E-07) | 8.461E-07 (-3.769E-07, 3.769E-07) | 1.431E-05 (-3.424E-06, 3.424E-06) | 1.626E-05 (-3.569E-06, 3.569E-06) | 3.738E-07 (-8.206E-08, 8.206E-08) |
| Phenol | $C_6H_6O$ | 6.494E-07 (-2.911E-07, 2.911E-07) | 3.912E-06 (-6.833E-07, 6.833E-07) | 2.971E-05 (-5.852E-06, 5.852E-06) | 1.555E-05 (-3.649E-06, 3.649E-06) | 4.529E-06 (-1.374E-06, 1.374E-06) |
| Phenylacetylene | $C_8H_6$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 5.649E-08 (-2.939E-08, 2.939E-08) | 0 (0, 0) |
| Styrene | $C_8H_8$ | 0 (0, 0) | 0 (0, 0) | 3.943E-06 (-6.496E-07, 6.496E-07) | 1.182E-05 (-4.332E-06, 4.332E-06) | 3.442E-07 (-2.149E-07, 2.149E-07) |
| 1,3,5-Cyclooctatriene | $C_8H_{10}$ | 1.631E-07 (-2.447E-07, 3.263E-07) | 4.304E-06 (-5.192E-06, 7.344E-06) | 2.197E-05 (-1.556E-05, 2.655E-05) | 5.734E-06 (-5.197E-06, 8.064E-06) | 0 (0, 0) |
| o-Xylene | $C_8H_{10}$ | 4.702E-07 (-5.407E-07, 5.407E-07) | 2.497E-06 (-7.558E-07, 7.558E-07) | 2.425E-05 (-4.617E-06, 4.617E-06) | 9.236E-06 (-1.429E-06, 1.429E-06) | 4.466E-07 (-2.264E-07, 2.264E-07) |
| Benzaldehyde | $C_7H_6O$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 6.349E-06 (-3.409E-06, 6.584E-06) | 1.767E-07 (-2.650E-07, 3.534E-07) |
| p-Benzoquinone | $C_6H_4O_2$ | 0 (0, 0) | 5.046E-07 (-7.569E-07, 1.009E-06) | 5.895E-06 (-4.490E-06, 7.437E-06) | 5.214E-06 (-5.862E-06, 8.469E-06) | 0 (0, 0) |
| Cresols | $C_7H_8O$ | 0 (0, 0) | 0 (0, 0) | 4.679E-06 (-2.511E-06, 2.511E-06) | 6.012E-06 (-4.367E-06, 4.367E-06) | 0 (0, 0) |
| Benzyl alcohol | $C_7H_8O$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 1.000E-06 (-1.501E-06, 2.001E-06) | 3.600E-07 (-3.457E-07, 5.257E-07) |
| 1,4-Cyclohex-2-enedione | $C_6H_6O_2$ | 0 (0, 0) | 0 (0, 0) | 8.403E-07 | 8.309E-07 | 0 (0, 0) |

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|---|---|---|---|---|---|---|
| | | | | (-8.438E-07, 1.264E-06) | (-1.246E-06, 1.662E-06) | |
| 1,4-Benzenediol | $C_6H_6O_2$ | 0 (0, 0) | 2.653E-06 (-1.026E-06, 1.026E-06) | 5.425E-06 (-1.152E-06, 1.152E-06) | 4.645E-06 (-1.650E-06, 1.650E-06) | 3.216E-06 (-1.101E-06, 1.101E-06) |
| Indene | $C_9H_8$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 2.695E-06 (-6.357E-07, 6.357E-07) | 0 (0, 0) |
| Indane | $C_9H_{10}$ | 0 (0, 0) | 0 (0, 0) | 3.183E-06 (-1.750E-06, 3.341E-06) | 6.242E-06 (-5.102E-06, 8.223E-06) | 6.838E-08 (-1.026E-07, 1.368E-07) |
| Methylbenzaldehydes | $C_8H_8O$ | 0 (0, 0) | 0 (0, 0) | 5.333E-06 (-8.816E-07, 8.816E-07) | 3.544E-06 (-1.009E-06, 1.009E-06) | 1.340E-07 (-1.541E-07, 1.541E-07) |
| 1,3,5-Trimethylbenzene | $C_9H_{12}$ | 0 (0, 0) | 0 (0, 0) | 9.349E-06 (-4.841E-06, 9.515E-06) | 2.883E-06 (-1.488E-06, 2.930E-06) | 1.931E-07 (-2.897E-07, 3.862E-07) |
| Dimethylphenols | $C_8H_{10}O$ | 0 (0, 0) | 2.900E-07 (-2.745E-07, 4.195E-07) | 1.193E-06 (-6.611E-07, 1.257E-06) | 9.944E-07 (-5.865E-07, 1.084E-06) | 2.036E-07 (-1.984E-07, 3.002E-07) |
| Naphthalene | $C_{10}H_8$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 2.796E-05 (-1.961E-05, 3.359E-05) | 1.294E-06 (-8.740E-07, 1.521E-06) |
| 1,2-Dihydronaphthalene | $C_{10}H_{10}$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 1.469E-06 (-7.617E-07, 1.496E-06) | 1.134E-08 (-1.700E-08, 2.267E-08) |
| 1,4,5,8-Tetrahydronaphthalene | $C_{10}H_{12}$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 1.966E-05 (-1.283E-05, 2.265E-05) | 3.598E-07 (-5.397E-07, 7.196E-07) |
| 2-Methylpropenylbenzene | $C_{10}H_{12}$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 1.964E-06 (-5.949E-07, 5.949E-07) | 0 (0, 0) |
| 1-Methylnaphthalene | $C_{11}H_{10}$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 8.429E-07 (-4.487E-07, 8.701E-07) | 6.261E-07 (-3.908E-07, 7.039E-07) |
| Biphenyl | $C_{12}H_{10}$ | 0 (0, 0) | 0 (0, 0) | 0 (0, 0) | 2.962E-07 (-1.985E-07, 3.466E-07) | 0 (0, 0) |

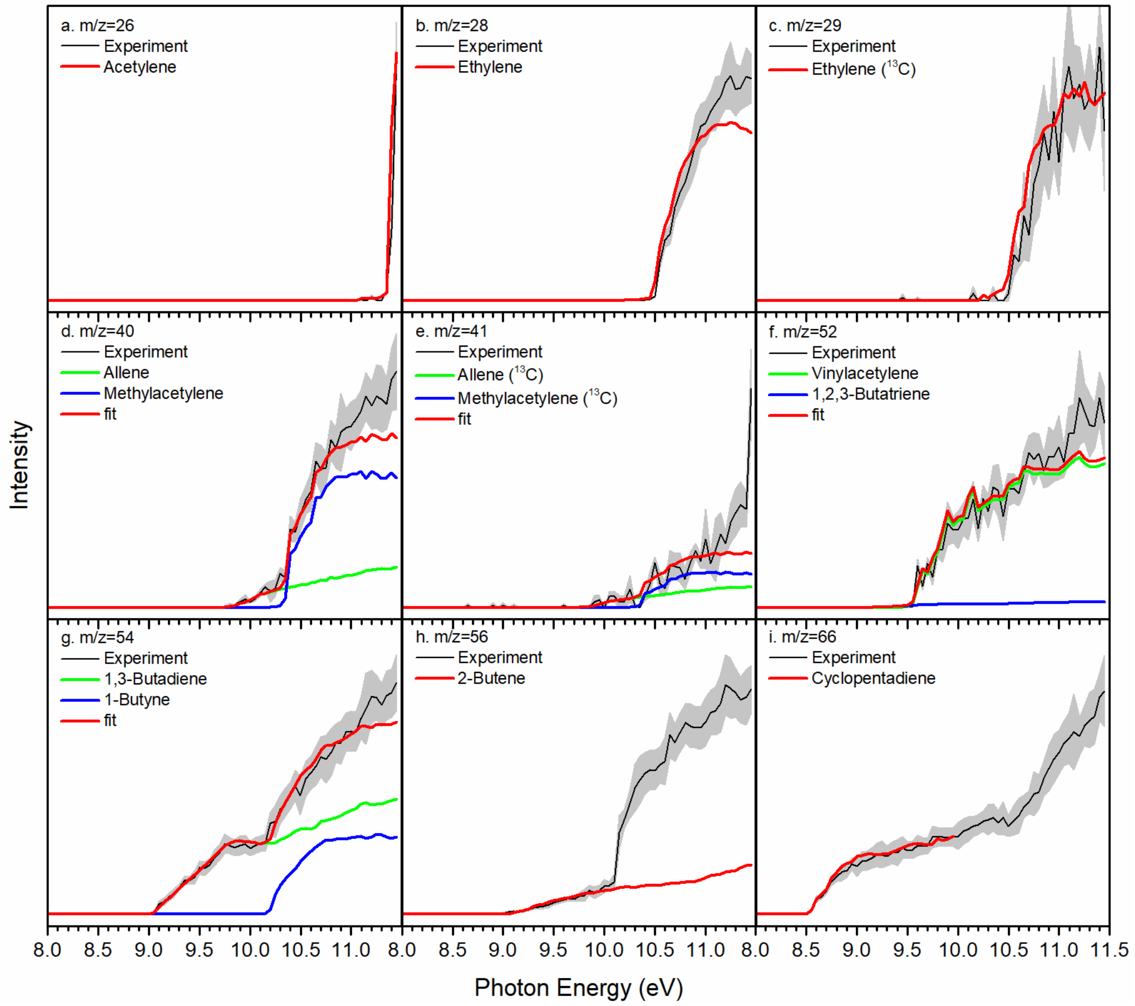

**Figure S1-1.** Experimental photoionization efficiency curves (PIE, black lines) for hydrocarbon species recorded from the oxidation of JP-10 at 1004 K along with the experimental errors (gray area) and the reference PIE curves (blue, green and red lines). In the case of multiple contributions to one PIE curve, the red line resembles the overall fit.

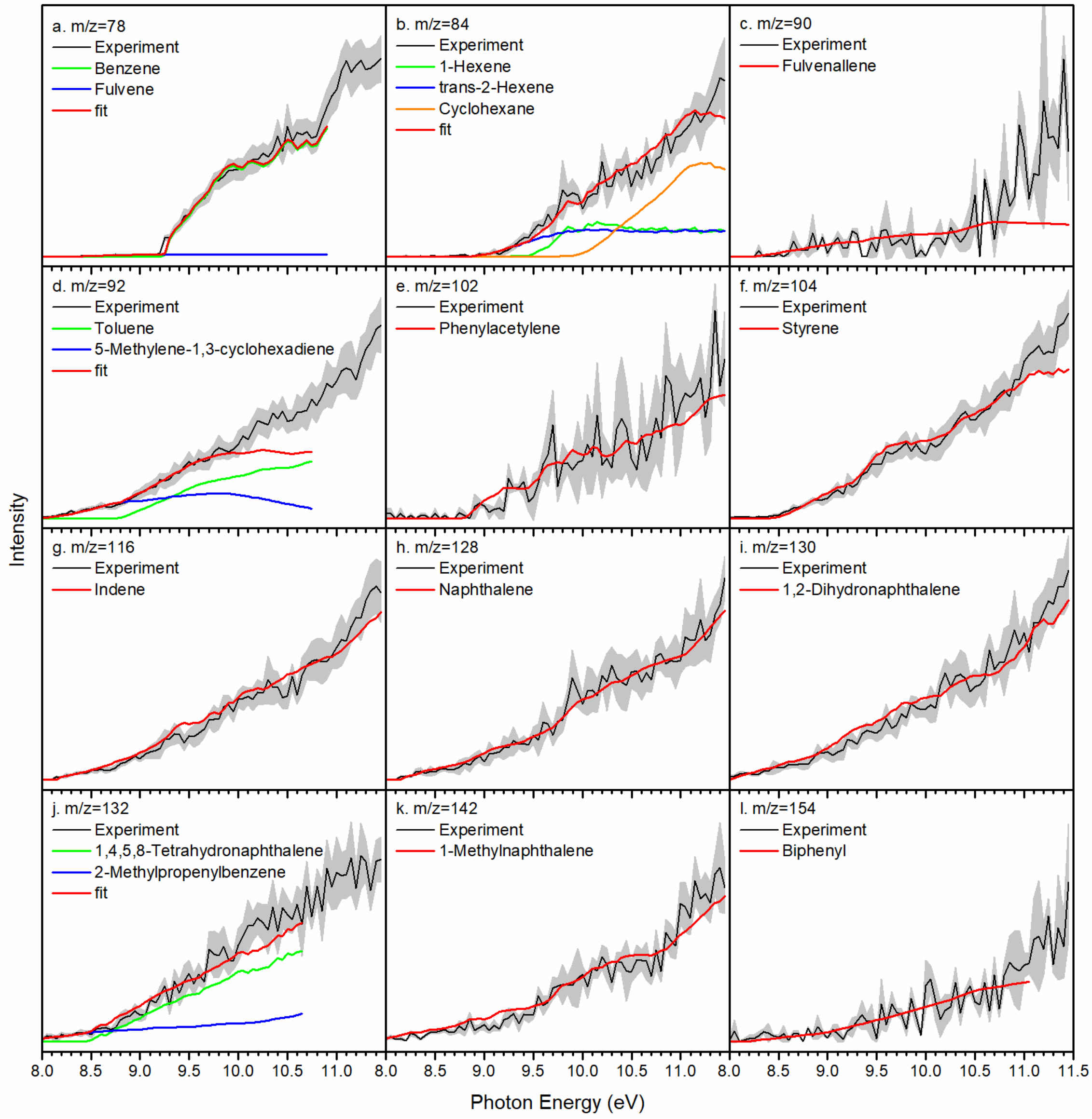

**Figure S1-2.** Experimental photoionization efficiency curves (PIE, black lines) for hydrocarbon species recorded from the oxidation of JP-10 at 1004 K along with the experimental errors (gray area) and the reference PIE curves (blue, green and red lines). In the case of multiple contributions to one PIE curve, the red line resembles the overall fit.

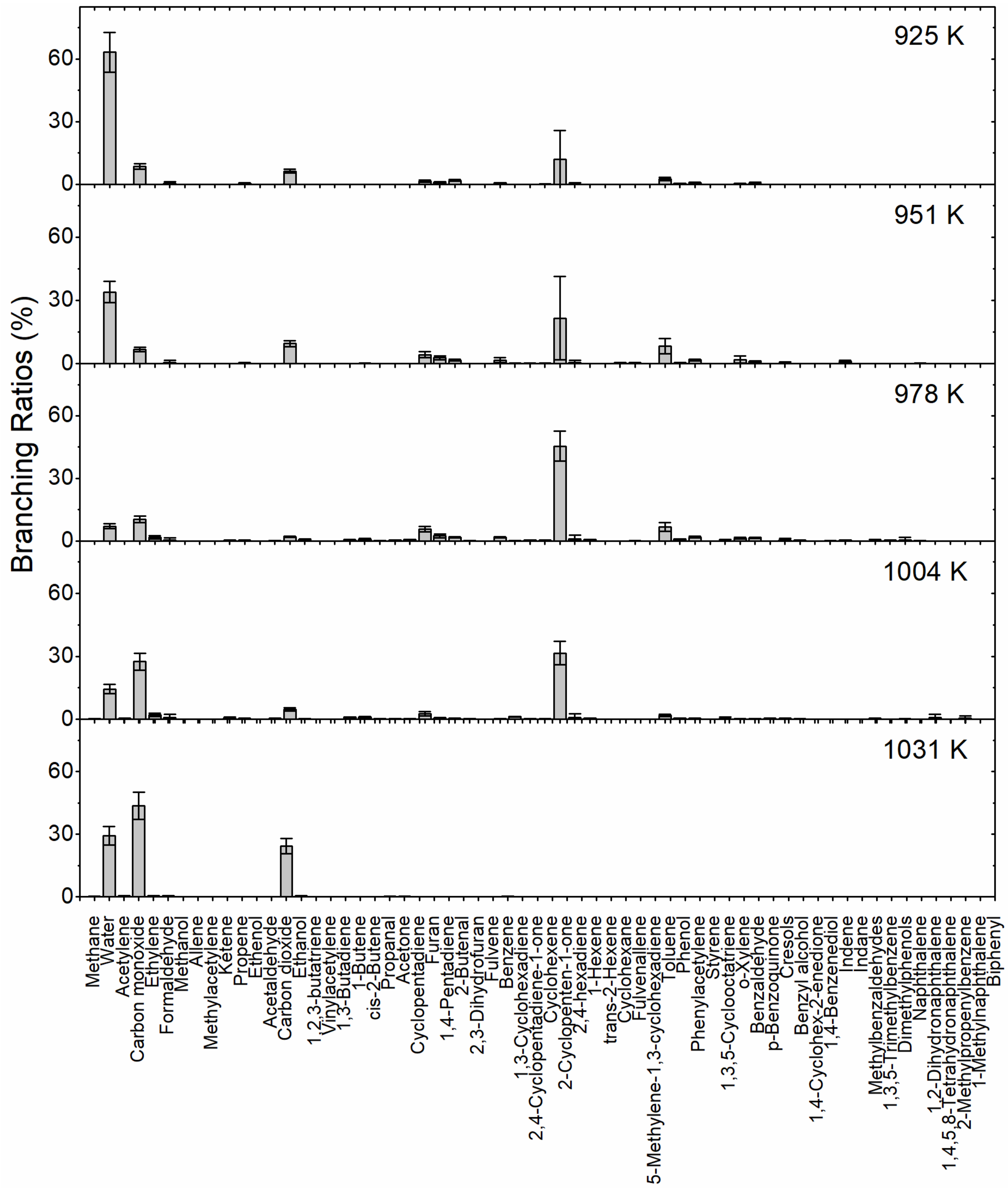

**Figure S2.** Overall branching ratios of the species obtained in the oxidation of JP-10 in temperatures range from 925 to 1031 K.

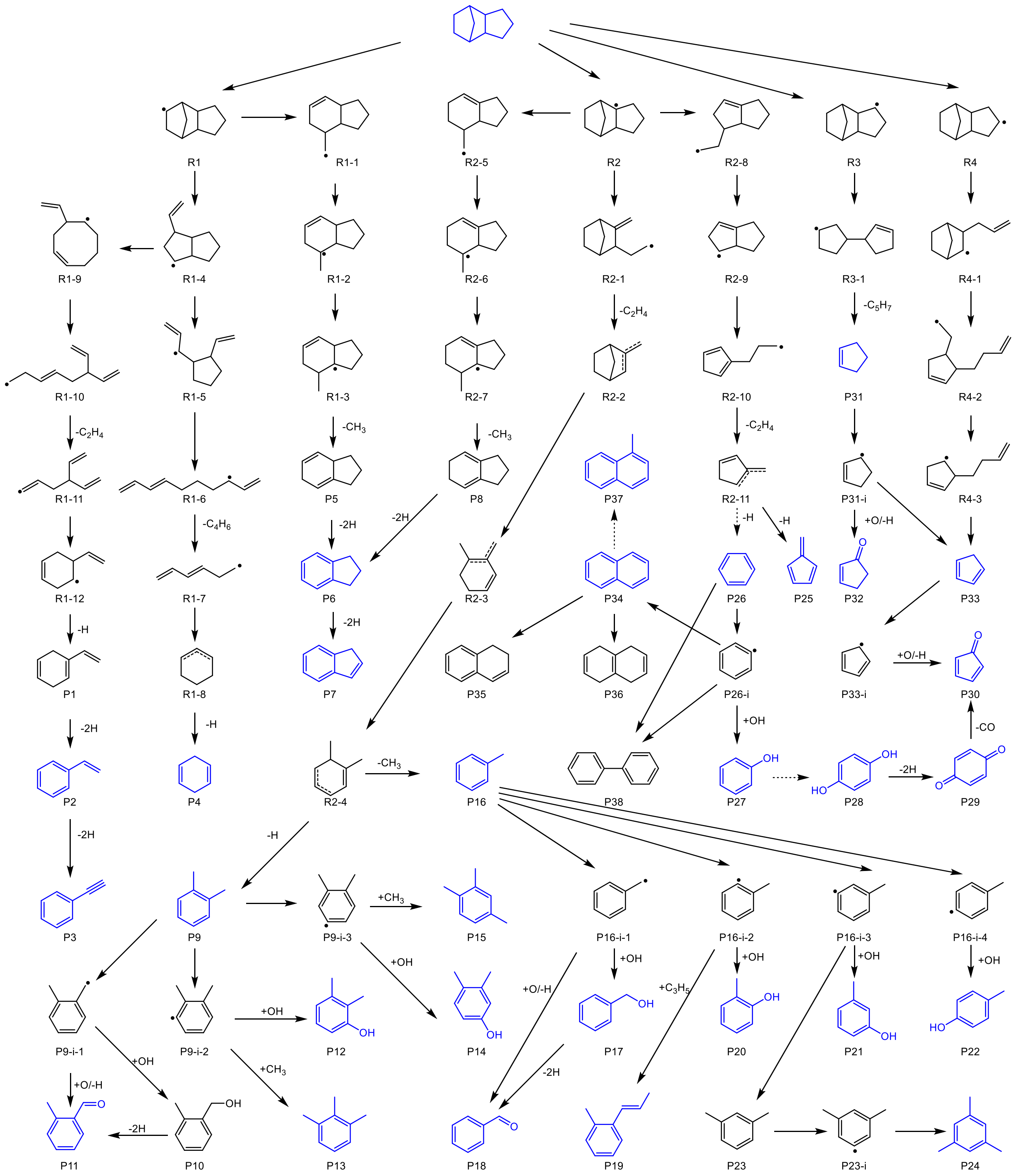

**Figure S3**. Proposed reaction mechanism for JP-10 oxidation. Due to the complex formation pathways for small species, only the intermediates/products with carbon atoms over five are presented. Species detected in this work are highlighted in blue.

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