Investigation of 2,5-dimethylfuran oxidation reaction initiated by O(^{3}P) atoms *via* synchrotron photoionization

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Introduction

Energy allows us to access convenient lifestyles. Owing to this provision of energy and the human population growth, the global demand for energy, which mostly relies on fossil fuels, is increasing rapidly.[1] More than 80% of this requirement has been fulfilling through fossil fuels, the limited thus depleting resource.[1-2] To reduce the usage of fossil fuels and meet the requirement, eclectic resources are being studied and biofuels have been receiving great attention. Among the candidates of biofuel, 2,5-dimethylfuran (2,5-DMF) attracts many researchers to investigate its properties. 2,5-DMF has a high volumetric energy density (31.5 MJ/L) compare to gasoline (32.2 MJ/L) with a high octane number (119).[3-4] Higher octane numbers tend to reduce knocking in an engine and thus increase fuel efficiency and lessen damages to the engine.[3] Due to its great potential as an alternative fuel, many studies regarding production and combustion of 2,5-DMF have been carried.

Our previous study probed methylidyne radical (CH and CD) reaction with 2,5-DMF and two main pathways, CH addition and isomerization assisted by a hydrogen atom, were reported.[5] In this work, oxidation of 2,5-DMF initiated by O(^{3}P) was studied at 550 and 700 K through synchrotron radiation coupled with multiplexed photoionization mass spectrometry at the Lawrence Berkeley National Laboratory (LBNL). The measured photoionization (PI) spectra and kinetic traces were utilized to identify products. Reaction mechanisms of all the identified products are presented employing the potential energy surface (PES) scan method and electronic structure calculations.

Methods

The Chemical Dynamics Beamline 9.0.2 at the Advanced Light Source (ALS) of LBNL was utilized to carry out this experiment.[6] Reaction species were identified through multiplexed time- and energy-resolved mass spectrometry coupled with tunable synchrotron radiation for photoionization. The collected data consisted of the ion signal as a function of photon energy (eV), reaction time (ms), and mass-to-charge ratio (*m/z*), which formed a three-dimensional data block (Figure 1).[7] Two-dimensional slices of the three-dimensional data were obtained for the data analysis by fixing one variable. The reactants show negative ion signal (depleting species) from kinetic time plots (ion signal vs kinetic time), whereas products have a positive signal. Figure 2 shows the time traces of the reactant (multiplied by -1) compared with a primary product and secondary products. The signal was integrated in the time range 0-40 ms to minimize the presence of secondary product signal at both temperatures.

Branching ratios of the products were calculated based on the following equation 1:

$$\text{Branching ratio} = \frac{C_P}{C_{P'}} = \frac{S_P\sigma_{P'}\delta_{P'}}{S_{P'}\sigma_P\delta_P} = \frac{S_P\sigma_{P'}(m_{P'})^{0.67}}{S_{P'}\sigma_P(m_P)^{0.67}} = \frac{S_P\sigma_{P'}}{S_{P'}\sigma_P}\text{MDF} \cdots\cdots (1)$$

where MDF represents for mass discrimination factor, P and P′ stand for products (where the prime subscript indicates the reference product, 3-penten-2-one), C_P and $C_{P'}$ are the concentrations, S_P and $S_{P'}$ are the measured signals from the PI spectra at a certain photon energy (11 eV in this study). The mass-dependent response (δ_P and $\delta_{P'}$) is approximately equal to the mass (m) of the identified species to the power of 0.67. The σ_P and $\sigma_{P'}$ are the energy dependent photoionization cross-section, which were estimated using the semiempirical model at 11.8 eV presented by Bobeldijk et al. The propagation uncertainty calculations were performed based on the uncertainties of cross-section from literatures and ion signal uncertainties in this work. Molecular structures of the identified species were optimized through the CBS-QB3 composite method[8-9] to obtain reliable zero-point vibrational energy corrected total electronic energies (E_0) that allow for calculation of various thermodynamic quantities, such adiabatic ionization energies and enthalpies of reaction. The B3LYP functional level of theory with the basis set of CBSB7 was used to calculate the harmonic vibrational frequencies to obtain simulated photoionization spectra based on Frank-Condon and Frank-Condon-Herzberg-Teller simulation.[10] The simulated and available literature photoelectron spectra are used to identify the detected products. The potential energy surface scan is utilized to investigate energy pathways, and Intrinsic Reaction Coordinate method is used to verify the pathways.[11]

Results

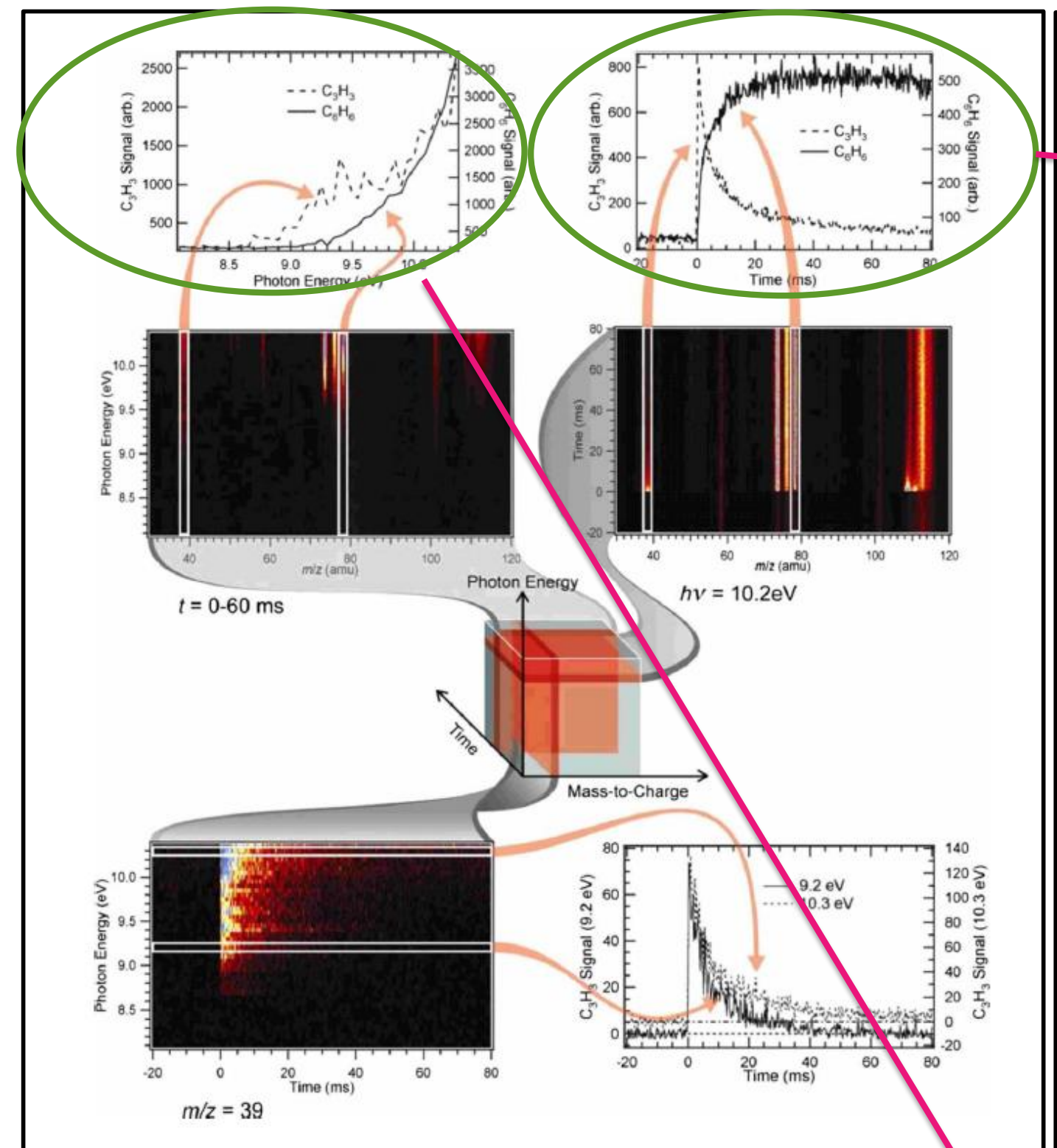


Figure 1. The three-dimensional dataset obtained at the ALS in Berkeley, CA.[7]

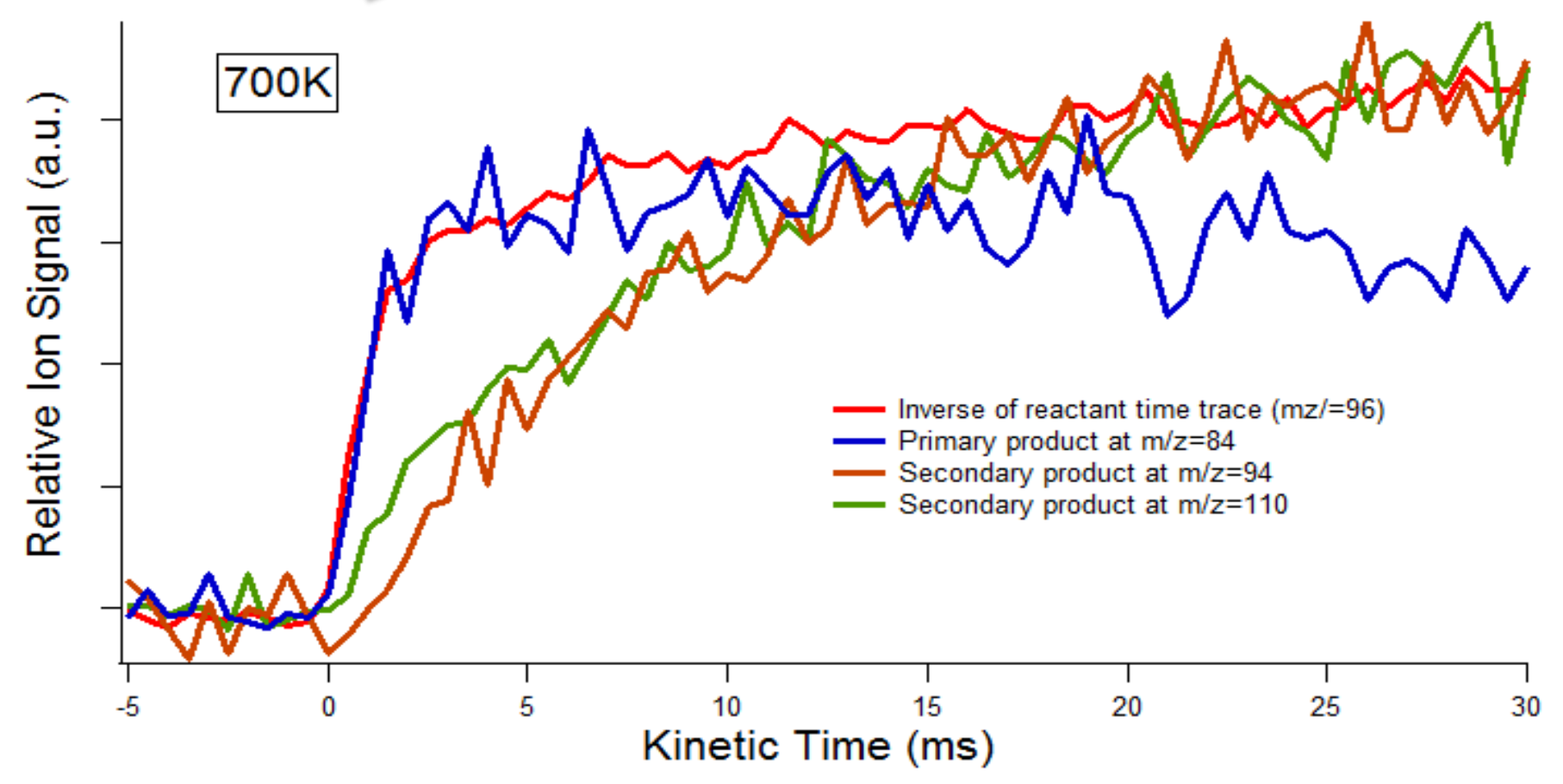
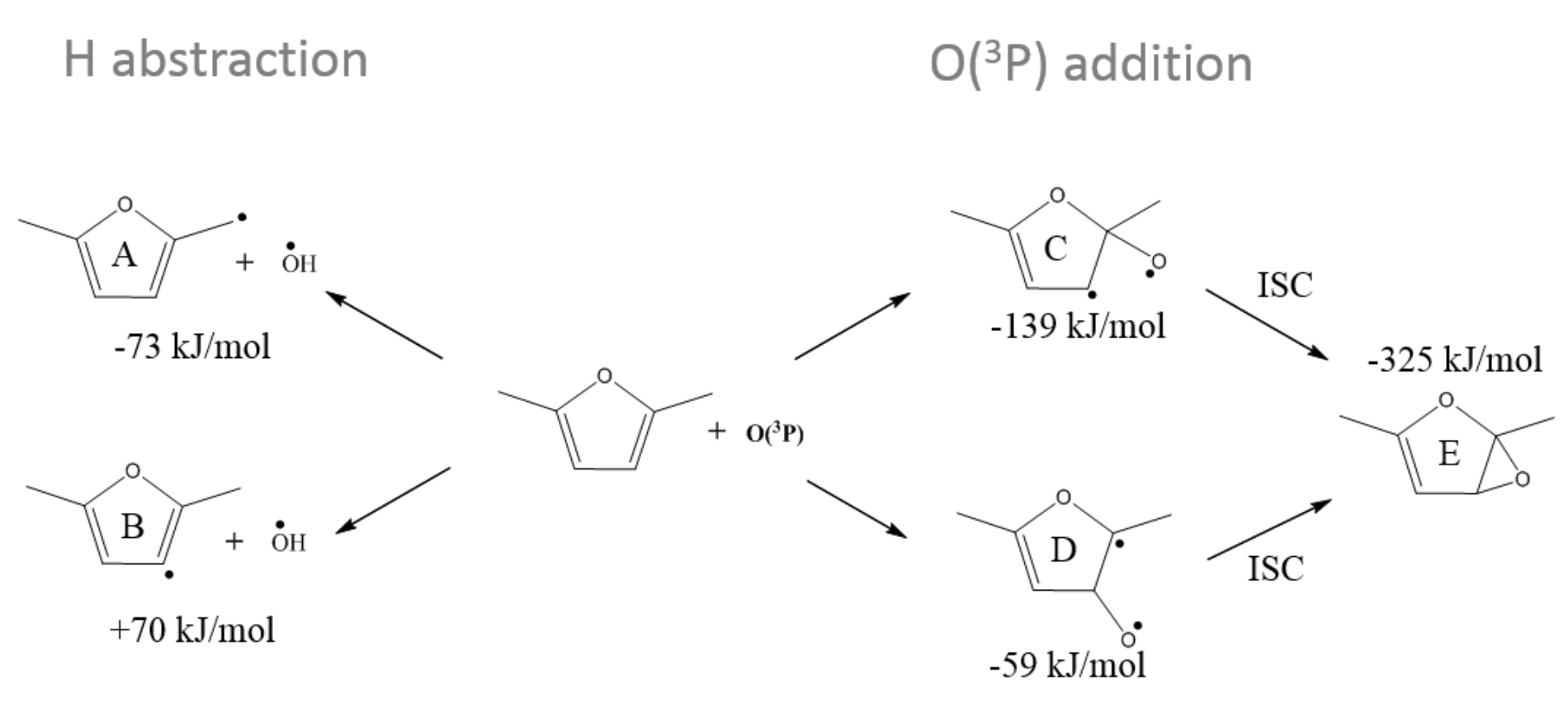


Figure 2. Time traces of reactant (inverted signal, i.e. multiplied by -1), primary, and secondary products at 700K.



Scheme 1. Reaction pathways for H abstraction and for O(^{3}P) addition. The energies of the presented species are relative to 2,5-DMF+ O(^{3}P).

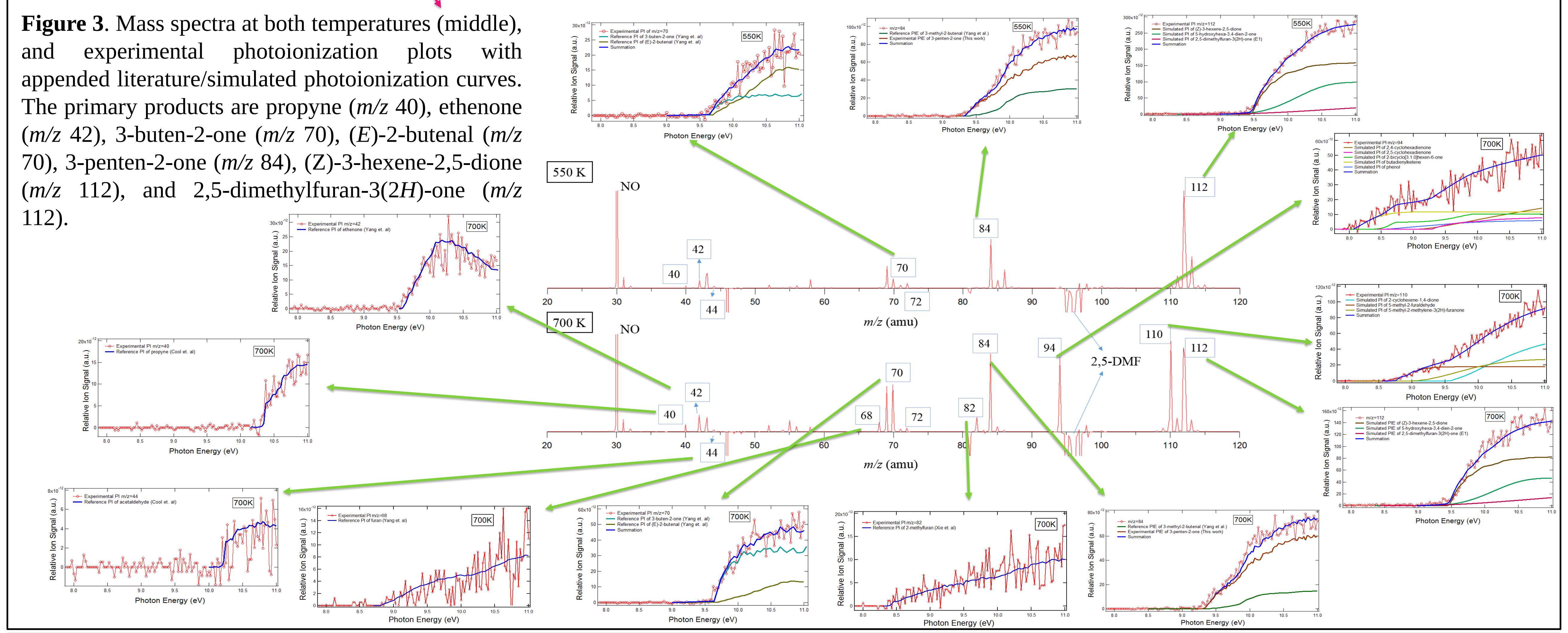


Figure 3. Mass spectra at both temperatures (middle), and experimental photoionization plots with appended literature/simulated photoionization curves. The primary products are propyne (*m/z* 40), ethenone (*m/z* 42), 3-buten-2-one (*m/z* 70), (*E*)-2-butenal (*m/z* 70), 3-penten-2-one (*m/z* 84), (Z)-3-hexene-2,5-dione (*m/z* 112), and 2,5-dimethylfuran-3(2*H*)-one (*m/z* 112).

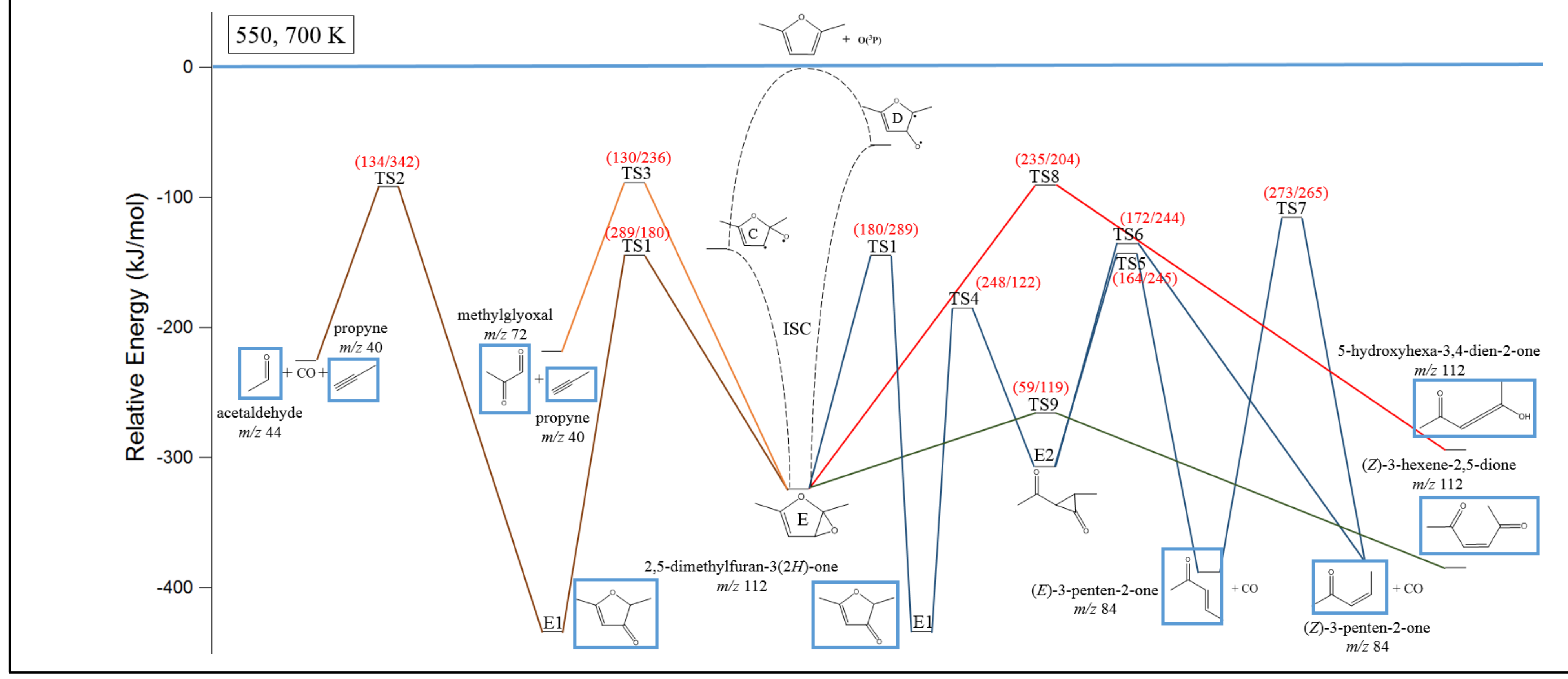


Figure 4. Reaction pathways of identified products formed from epoxide E at both temperatures. The relative energies of transition states compared to the adjacent intermediates are indicated in the parentheses. The left value corresponds to the energy barrier for the intermediate located on the left side whereas the right value is for the other intermediate. Identified molecules are highlighted with blue boxes.

Table 1. Branching ratios of the identified products that show fast forming rate at either/both temperatures relative to 3-penten-2-one.

m/z	Species	Branching ratios and uncertainties 550 K	700 K
40	propyne	0.17 ± 0.07	0.37 ± 0.13
42	ethenone	0.59 ± 0.21	0.91 ± 0.29
70	3-buten-2-one	0.42 ± 0.14	2.52 ± 0.81
70	(*E*)-2-butenal	0.72 ± 0.23	0.72 ± 0.23
84	3-penten-2-one	1.00 ± 0.30	1.00 ± 0.30
84	3-methyl-2-butenal	0.80 ± 0.24	0.43 ± 0.13
112	(*Z*)-3-hexene-2,5-dione	1.28 ± 0.40	0.78 ± 0.23
112	5-hydroxyhexa-3,4-dien-2-one	0.82 ± 0.25	0.46 ± 0.13
112	2,5-dimethylfuran-3(2*H*)-one	0.15 ± 0.05	0.12 ± 0.03

Conclusions

In this investigation, oxidation of 2,5-dimethylfuran initiated by O(^{3}P) was studied employing synchrotron radiation at the Lawrence Berkeley National Laboratory. A theoretical study was also performed to probe primary chemistry reaction pathways. Products branching ratios were calculated compared to 3-penten-2-one (set the 3-penten-2-one as 1.00) based on Equation 1. We observed two main reaction pathways, O(^{3}P) addition and hydrogen subtraction. The O(^{3}P) addition pathway, more favorable than hydrogen abstraction, forms two triplet diradicals (C and D), which undergo intersystem crossing into the singlet epoxide E. The hydrogen abstraction pathway generates only the doublet radical (A). In fact, the formation of the radical (B) is endothermic. An oxygen molecule then binds to A to generate products. From our previous study of the Cl initiated oxidation of 2-methylfuran the main expected product from this channel derives from the self-reaction of the peroxy radical and should be 5-methylfurfural, which is indeed observed. The experimental PI spectra of products in this work were identified by comparison with literature PI spectra and/or simulated PI spectra. The identified molecules at the both temperatures are propyne (*m/z* 40), ethenone (*m/z* 42), acetaldehyde (*m/z* 44), 2-proen-1-ol (*m/z* 58), 3-buten-2-one (*m/z* 70), (*E*)-2-butenal (*m/z* 70), 3-methyl-2-butenal (*m/z* 84), 3-penten-2-one (*m/z* 84), (Z)-3-hexene-2,5-dione (*m/z* 112), 5-hydroxyhexa-3,4-dien-2-one (*m/z* 112), and 2,5-dimethylfuran-3(2*H*)-one (*m/z* 112). At 700 K additional product masses were detected, *m/z* 68, 82, 94 and 110, and identified as non-primary products based on their time traces.

Acknowledgments

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