

MEASURING HYDROPEROXIDE CHAIN-BRANCHING AGENTS DURING N-PENTANE LOW-TEMPERATURE OXIDATION

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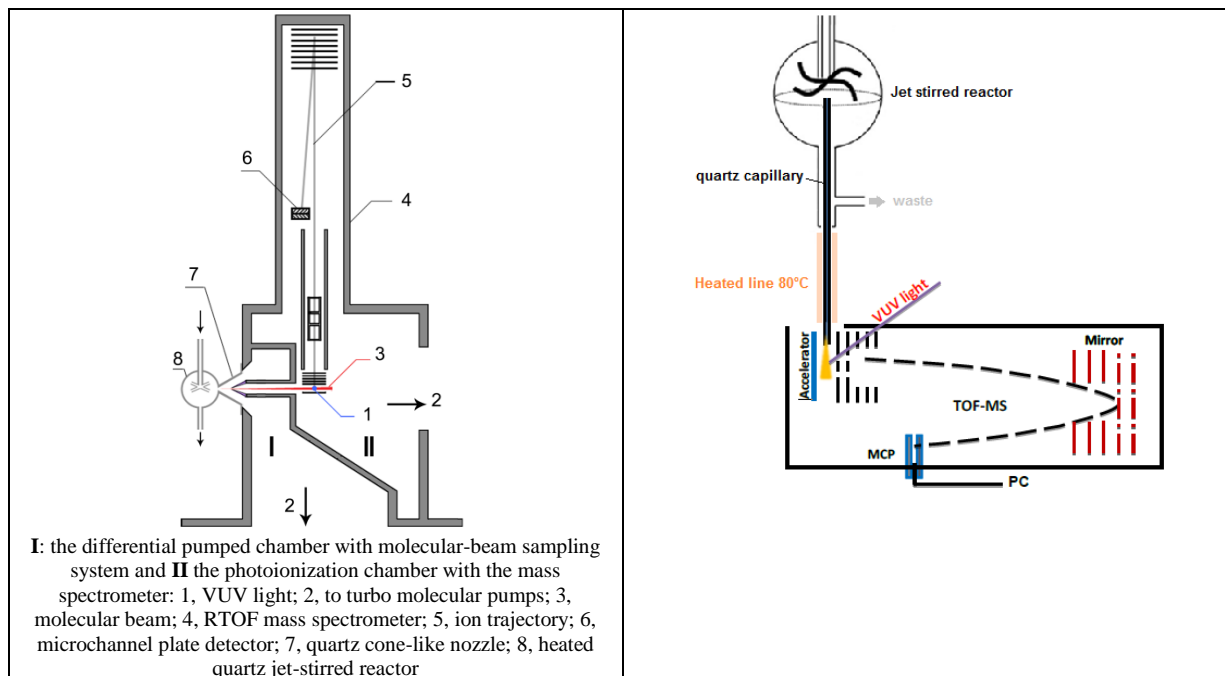
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SUPPLEMENTARY DESCRIPTION

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1/ Additional details about the used experimental devices and methods

1a/ Schemes of the apparatuses coupling JSR to time-of-flight mass spectrometers combined with synchrotron and laser photoionization



Schematic diagram of the instruments including the jet-stirred reactor and in (a) the synchrotron VUV photoionization mass spectrometer and in (b) the laser photoionization mass spectrometer.

1b/ Method used for calculating mole fraction from mass spectrometer ion signal

As described by Cool et al. [1], for time-of-flight mass spectrometry combined with tunable synchrotron photoionization with molecular-beam sampling, the ion signal (integrated ion count $S_i(T)$) for a species of mass i may be written as:

$$S_i(T) = CX_i(T)\sigma_i(E)D_i\Phi_p(E)F(T) \quad (1)$$

With: C: Constant of proportionality,

$X_i(T)$: Mole fraction of the species at the temperature T ,

$\sigma_i(E)$: Photoionization cross-section at the photon energy E ,

D_i : Mass discrimination factor,

$\Phi_p(E)$: Photon flux,

$F(T)$: Empirical instrumental sampling function, which relates the molecular beam molar density in the ionization region to the temperature and pressure inside the reactor.

Because $F(T)$ is the same for all component species, we have for a given species, at a given ionization energy:

$$X_i(T) = X_i(560K) \times \left[\frac{S_i(T)}{S_i(560K)} \cdot \frac{F(560K)}{F(T)} \right] \quad (2)$$

The values $F(560K)/F(T)$ can be deduced from the ion signal obtained at a photon energy of 16.20 eV for argon (mass = 40 g/mol) which acted as an internal standard.

$$\frac{F(T)}{F(560K)} = \frac{S_{40}(T)}{S_{40}(560K)} = FKT \quad (3)$$

In our experiments, the values of this parameter vary from 1 at 560 K to 0.747 at 780 K.

To know the complete evolution with temperature of the experimental mole fraction of a species, it is then only necessary to have a calibration at one given temperature. The mole fractions of *n*-pentane were then directly derived from the ion signals normalized by FTK at m/z 70 considering that no reaction occurred below 590 K.

It can be deduced from equation (1), that the mole fraction of a species of mass i can be obtained from that of a reference species, of mass ref , at a given temperature and energy:

$$\frac{S_i(T)}{S_{ref}(T)} = \frac{X_i(T)}{X_{ref}(T)} \cdot \frac{\sigma_i(T)}{\sigma_{ref}(T)} \cdot \frac{D_i(T)}{D_{ref}(T)} \quad (4)$$

For time-of-flight mass spectrometry combined with laser ionization with capillary tube

sampling, equation (1) can still be used. However the comparison of the shape of the signal temperature evolutions with those obtained by gas chromatography indicates no variation of FTK with temperature. Therefore no calibration with an internal standard was used. Calibrations made by sampling pure compounds of different masses have shown that a constant value of D_i equal to 1 can be used whatever the mass of the species. For this apparatus, the mole fraction of a species of mass i can be obtained from that of a reference species, of mass ref , at a given temperature and the laser energy by the simplified equation:

$$\frac{S_i(T)}{S_{ref}(T)} = \frac{X_i(T)}{X_{ref}(T)} \cdot \frac{\sigma_i(T)}{\sigma_{ref}(T)} \quad (5)$$

Cross sections used for the quantification of species detected by mass spectrometry

As a reminder, the following ionization energies have been used:

- 10.6 eV for laser photoionization
- 11.0, 13.0 or 16.6 eV for SVUV-photoionization.

Compound name	Formula	m/z	IE (eV)	σ (Mb)		Reference
				at 10.6 eV	at 11.0 eV	
Ketohydroperoxide	C ₅ H ₁₀ O ₃	118	≈9.3	14.59	20.55	<i>Estimated*</i>
Hydroxyperoxy-pentane	C ₅ H ₁₂ O ₂	104	9.34	7.26	15.09	<i>Estimated*</i>
Pentyl-hydroperoxide	C ₅ H ₁₀ O ₂	102	-	17.16	22.50	<i>Estimated*</i>
Pentadiones	C ₅ H ₈ O ₂	100	≈9.1	17.58	20.92	<i>Estimated*</i>
Butyl-hydroperoxide	C ₄ H ₈ O ₂	88	-	16.43	20.00	<i>Estimated*</i>
Propyl-hydroperoxide	C ₃ H ₆ O ₂	74	-	15.71	17.50	<i>Estimated*</i>
<i>n</i> -pentane	C ₅ H ₁₂	72	10.28		12.75	<i>Zhou et al. [2]</i>
Ethyl-hydroperoxide	C ₂ H ₆ O ₂	62	9.61	5.07	7.59	<i>Estimated*</i>
Acetic acid	C ₂ H ₄ O ₂	60	10.65	-	6.81	<i>Herbinet et al. [3]</i>
Methyl-hydroperoxide	CH ₄ O ₂	48	9.84	4.35	5.09	<i>Estimated*</i>
Acetaldehyde	C ₂ H ₄ O	44	10.229	8.06	7.96	<i>Cool et al. [4]</i>
Propene	C ₃ H ₆	42	9.73	11.36	9.73	<i>Cool et al. [4]</i>
Ketene	C ₂ H ₂ O	42	9.62	22.52	15.81	<i>Yang et al. [5]</i>
Formaldehyde	CH ₂ O	30	10.88	-	9.02	<i>Cooper et al. [6]</i>
Ethylene	C ₂ H ₄	28	10.5138	-	7.79	<i>Cool et al. [7]</i>

* see below for the method used the estimation of cross sections

CO (IE of 14.014 eV), CO₂ (IE of 13.777 eV), and water (IE of 12.66) detected using SVUV-PIMS were quantified using the signal of argon recorded at 16.6 eV as reference.

H₂O₂ (IE of 10.62 eV) detected using SVUV-PIMS was quantified at 13 eV, using the experimental cross section from Dodson et al. [8] ($\sigma = 36.46$ Mb) and the signal of pentane as reference.

Method for the estimation of cross sections

For compounds for which we haven't found the cross section in the literature, we had to make an estimate. This estimation method is based on the group additivity method proposed by Bobeldijk et al. [9]. Groups are defined as atom pairs in the considered molecules.

The value of each group is estimated from published data of known species at a given photon energy. From there, we simply sum each group constituting the related molecule in order to estimate its cross section.

cross section of atom pairs at 10.6 eV

group	σ (Mb)	compound	Reference
C-C	0.7275	<i>n</i> -pentane	<i>Zhou et al. [2]</i>
C=C	10.633	Propene	<i>Cool et al. [4]</i>
C-O	4.345	Dimethyl-ether	<i>Cool et al. [7]</i>
C=O	7.3325	Acetaldehyde	<i>Cool et al. [4]</i>
C-H, O-H or O-O	0		

cross section of atom pairs at 11 eV

group	σ (Mb)	compound	Reference
C-C	2.5	<i>butane</i>	<i>Wang et al. [10]</i>
C=C	9.91	Propene	<i>Cool et al. [4]</i>
C-O	5.085	Dimethyl-ether	<i>Cool et al. [7]</i>
C=O	5.46	Acetaldehyde	<i>Cool et al. [4]</i>
C-H, O-H or O-O	0		

As an example, we have for the C₅ ketohydroperoxides:

$$\sigma_{keto} = 4. \sigma_{C-C} + 1. \sigma_{C-O} + 1. \sigma_{C=O}$$

$$\sigma_{keto}(10.6 \text{ eV}) = 4 \times 0.7275 + 4.345 + 7.3325 = 14.59 \text{ Mb}$$

$$\sigma_{keto}(11 \text{ eV}) = 4 \times 2.5 + 5.085 + 5.46 = 20.55 \text{ Mb}$$

1c/ Description of the cw-CRDS analyses and the related quantification method

As described by Bahrini et al. [11], the near-infrared beam was provided by a fibred distributed feed-back (DFB) diode laser (Fitel-Furukawa FOL15DCWB-A81-W1509) emitting up to 40 mW, the wavelength can be varied in the range $6640 \pm 13 \text{ cm}^{-1}$ through changing the current applied to the diode laser. The diode laser emission is directly fibred and passes through a fibred optical isolator and a fibred acousto-optical modulator (AOM, AA Opto-Electronic). The AOM allows the laser beam to be deviated within 350 ns with respect to a trigger signal for a total duration of 1.5 ms. The zero-order beam is connected to a fibred optical wave meter (228 Bristol Instruments) for monitoring the wavelength of the laser emission with an accuracy of 0.01 cm^{-1} . The main first-order laser beam is coupled into the CRDS optical cavity through a short-focal-length lens ($f = 10 \text{ mm}$) for mode matching so as to excite the fundamental TEM_{00} mode. Two folding micrometric mirrors allow easy alignment of the beam, as shown in Figure S1.

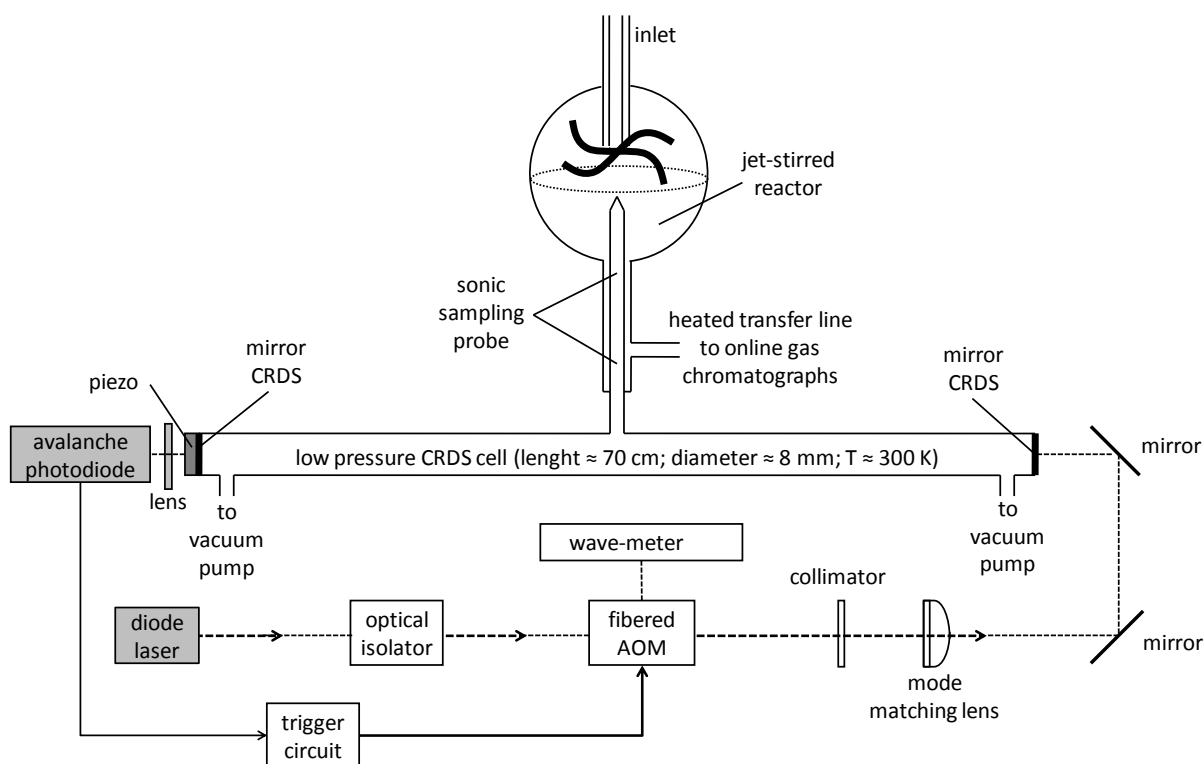


Figure S2: Schematic view of the experimental set-up (AOM= Acousto-optical modulator).

After many round trips, the optical signal transmitted through the cavity is converted into current by an avalanche photodiode (Perkin Elmer C30662E). A lab-designed amplifier-

threshold circuit converts the current signal to an exploitable voltage signal and triggers the AOM to deviate the laser beam (turn off of the first order) as soon as the cavity comes into resonance and the photodiode signal is connected to a fast 16-bit analogue acquisition card (PCI-6259, National Instruments) in a PC, which is triggered also by the amplifier-threshold circuit. The acquisition card has an acquisition frequency of 1.25 MHz, and thus the ring-down signal is sampled every 800 ns and the data are transferred to PC in real time. The ring-down time τ is obtained by fitting the exponential decay over a time range of seven lifetimes by a Levenberg-Marquardt exponential fit in LabView.

The concentration of a species being formed or consumed during the hydrocarbon oxidation process in a jet-stirred reactor (JSR), can be obtained by measuring the ring-down time of the empty cavity τ_0 (i.e., the ring-down time before heating the reactor) and the ring-down time τ , when performing an experiment at a given temperature:

$$\alpha = [A] \times \sigma = \frac{R_L}{c} \left(\frac{1}{\tau} - \frac{1}{\tau_0} \right) \quad (1)$$

where σ is the absorption cross section, R_L is the ratio between the cavity length L (i.e., the distance between the two cavity mirrors to the length L_A over which the absorber is present; see section on CH₄ quantification), and c is the speed of light. Knowing the absorption cross section σ , one can extract the concentration $[A]$ of the target molecule.

Table S1: Absorption lines and cross sections used for the quantification of formaldehyde, water and hydrogen peroxide.

	wavenumber ν (cm ⁻¹)	cross section σ (cm ²)	reference
CH ₂ O	6639.33	3.60x10 ⁻²²	Morajkar et al. [12]
	6641.67	4.59x10 ⁻²²	
H ₂ O	6638.9*	4.46x10 ⁻²³	Macko et al. [13]
	6640.9	1.60x10 ⁻²²	
	6641.27*	1.82x10 ⁻²²	
H ₂ O ₂	6639.26	7.62x10 ⁻²³	Parker et al. [14]
	6640.06	1.41x10 ⁻²²	
C ₂ H ₄	6638.33	4.05x10 ⁻²³	Bahrini et al. [11]
	6641.23	2.95x10 ⁻²³	

* These lines were used only at high temperature because they were perturbed by another peak at low-temperature resulting in uncertainties.

2/ Tested changes in the mechanism of Galway [15]

Diones formation

Initial mechanism

NC5KET13+OH=>NC5DIONE13+OH+H2O +1.000000E+012 +0.000000E+000 +0.000000E+000
NC5KET24+OH=>NC5DIONE24+OH+H2O +1.000000E+012 +0.000000E+000 +0.000000E+000
NC5KET31+OH=>NC5DIONE13+OH+H2O +2.000000E+012 +0.000000E+000 +0.000000E+000

With reactions derived from the Milano mechanisms [15]

O2+NC5KET..=>HO2+C5DIONE+OH +0.121700E+07 +2.000000E+000 +3.857096E+004
H+NC5KET..=>H2+C5DIONE+OH +0.171900E+07 +2.000000E+000 +2.663076E+003
OH+NC5KET..=>H2O+C5DIONE+OH +0.285300E+06 +2.000000E+000 -3.152530E+003
O+NC5KET..=>OH+C5DIONE+OH +0.096600E+07 +2.000000E+000 +1.356530E+003
HO2+NC5KET..=>H2O2+C5DIONE+OH +0.384900E+05 +2.000000E+000 +1.031880E+004
HCO+NC5KET..=>CH2O+C5DIONE+OH +0.090200E+06 +2.000000E+000 +1.077787E+004
CH3+NC5KET..=>CH4+C5DIONE+OH +0.278800E+05 +2.000000E+000 +3.544160E+003
CH3O+NC5KET..=>CH3OH+C5DIONE+OH +0.305700E+05 +2.000000E+000 +4.125500E+002
CH3O2+NC5KET..=>CH3O2H+C5DIONE+OH +0.543600E+05 +2.000000E+000 +1.077800E+004

- **Added reactions for the formation of C₄-C₅ alkenylhydroperoxides**

C4H71-3+HO2<=>C4H71-3OOH +1.000000E+011 +0.000000E+000 +0.000000E+000
PLOG / +1.000000E-002 +1.910000E+031 -7.230000E+000 +1.336200E+003 /
PLOG / +1.000000E-001 +6.310000E+042 -1.030000E+001 +5.568900E+003 /
PLOG / +1.000000E+000 +1.030000E+045 -1.060000E+001 +7.851500E+003 /
PLOG / +1.000000E+001 +2.790000E+037 -7.920000E+000 +6.497900E+003 /
PLOG / +1.000000E+002 +1.440000E+032 -6.010000E+000 +6.053600E+003 /

C4H71-3+HO2<=>C4H72-1OOH +1.000000E+011 +0.000000E+000 +0.000000E+000
PLOG / +1.000000E-002 +1.910000E+031 -7.230000E+000 +1.336200E+003 /
PLOG / +1.000000E-001 +6.310000E+042 -1.030000E+001 +5.568900E+003 /
PLOG / +1.000000E+000 +1.030000E+045 -1.060000E+001 +7.851500E+003 /
PLOG / +1.000000E+001 +2.790000E+037 -7.920000E+000 +6.497900E+003 /
PLOG / +1.000000E+002 +1.440000E+032 -6.010000E+000 +6.053600E+003 /

C5H91-3+HO2<=>C5H91-3OOH +1.000000E+011 +0.000000E+000 +0.000000E+000
PLOG / +1.000000E-002 +1.910000E+031 -7.230000E+000 +1.336200E+003 /
PLOG / +1.000000E-001 +6.310000E+042 -1.030000E+001 +5.568900E+003 /
PLOG / +1.000000E+000 +1.030000E+045 -1.060000E+001 +7.851500E+003 /
PLOG / +1.000000E+001 +2.790000E+037 -7.920000E+000 +6.497900E+003 /
PLOG / +1.000000E+002 +1.440000E+032 -6.010000E+000 +6.053600E+003 /

C5H91-3+HO2<=>C5H92-1OOH +1.000000E+011 +0.000000E+000 +0.000000E+000
PLOG / +1.000000E-002 +1.910000E+031 -7.230000E+000 +1.336200E+003 /
PLOG / +1.000000E-001 +6.310000E+042 -1.030000E+001 +5.568900E+003 /
PLOG / +1.000000E+000 +1.030000E+045 -1.060000E+001 +7.851500E+003 /
PLOG / +1.000000E+001 +2.790000E+037 -7.920000E+000 +6.497900E+003 /
PLOG / +1.000000E+002 +1.440000E+032 -6.010000E+000 +6.053600E+003 /

C5H92-4+HO2<=>C5H92-4OOH +1.000000E+011 +0.000000E+000 +0.000000E+000
PLOG / +1.000000E-002 +1.910000E+031 -7.230000E+000 +1.336200E+003 /
PLOG / +1.000000E-001 +6.310000E+042 -1.030000E+001 +5.568900E+003 /
PLOG / +1.000000E+000 +1.030000E+045 -1.060000E+001 +7.851500E+003 /
PLOG / +1.000000E+001 +2.790000E+037 -7.920000E+000 +6.497900E+003 /

PLOG / +1.0000000E+002 +1.4400000E+032 -6.0100000E+000 +6.0536000E+003 /

C5H92-4+HO2<=>C5H92-1OOH +1.0000000E+011 +0.0000000E+000 +0.0000000E+000

PLOG / +1.0000000E-002 +1.9100000E+031 -7.2300000E+000 +1.3362000E+003 /

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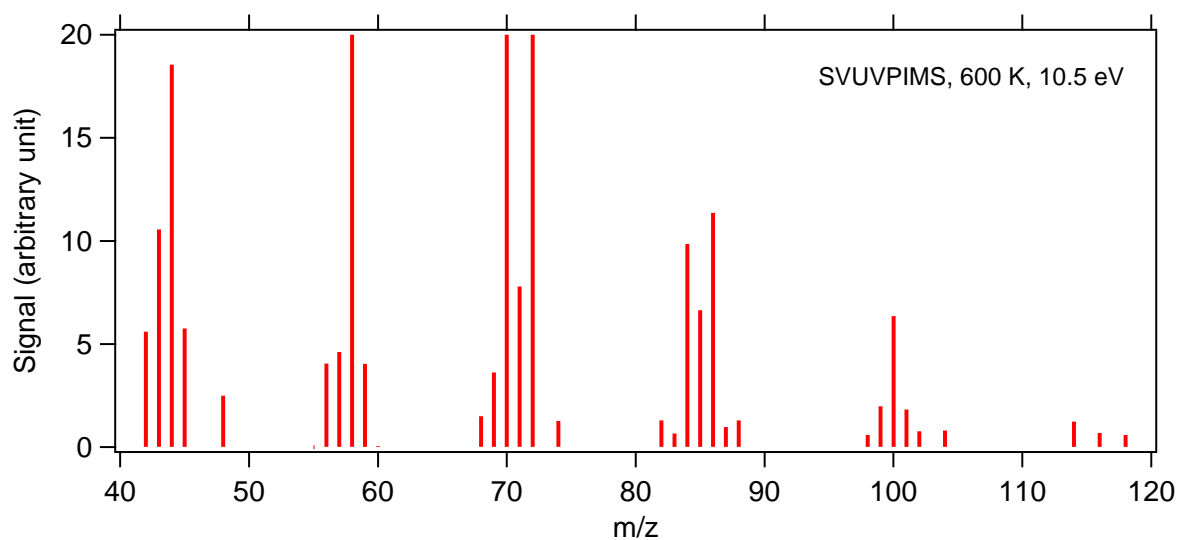
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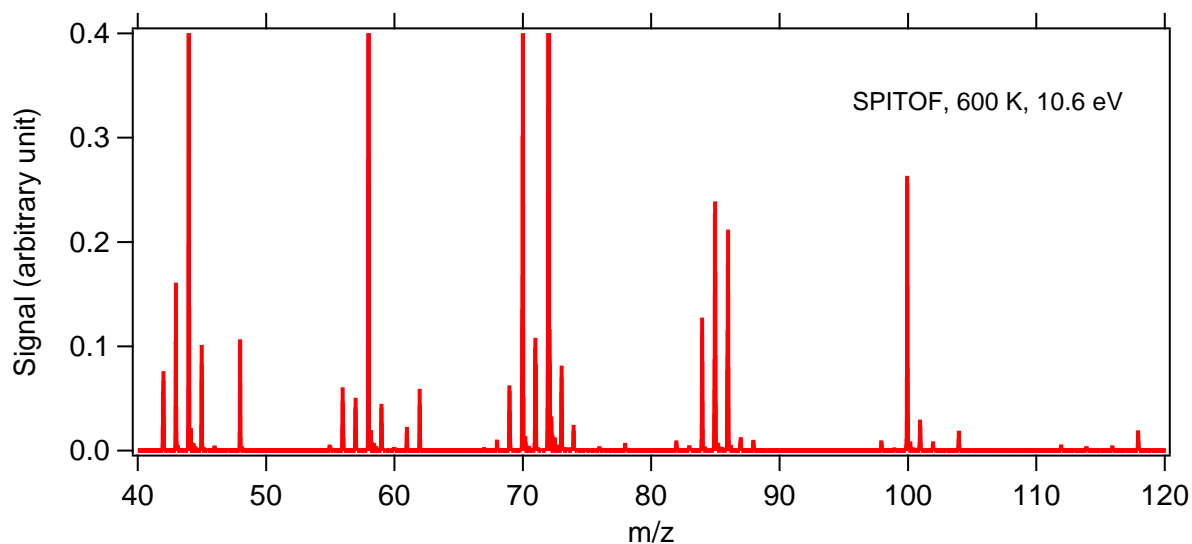
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3/ Comparisons of results obtained using several experimental techniques

3a/ Comparison of the mass spectra obtained with both types of mass spectrometer



(a)



(b)

Figure S3: Mass spectrum obtained during the stoichiometric n-pentane/O₂ oxidation at 600 K using mass spectrometers with (a) SVUV photoionization in Hefei and (b) laser photoionization in Nancy.

3b/ Temperature evolutions of the mole fractions of the species quantified by synchrotron VUV photoionization mass spectrometry, which are not shown in the text – Comparisons with other analytical techniques

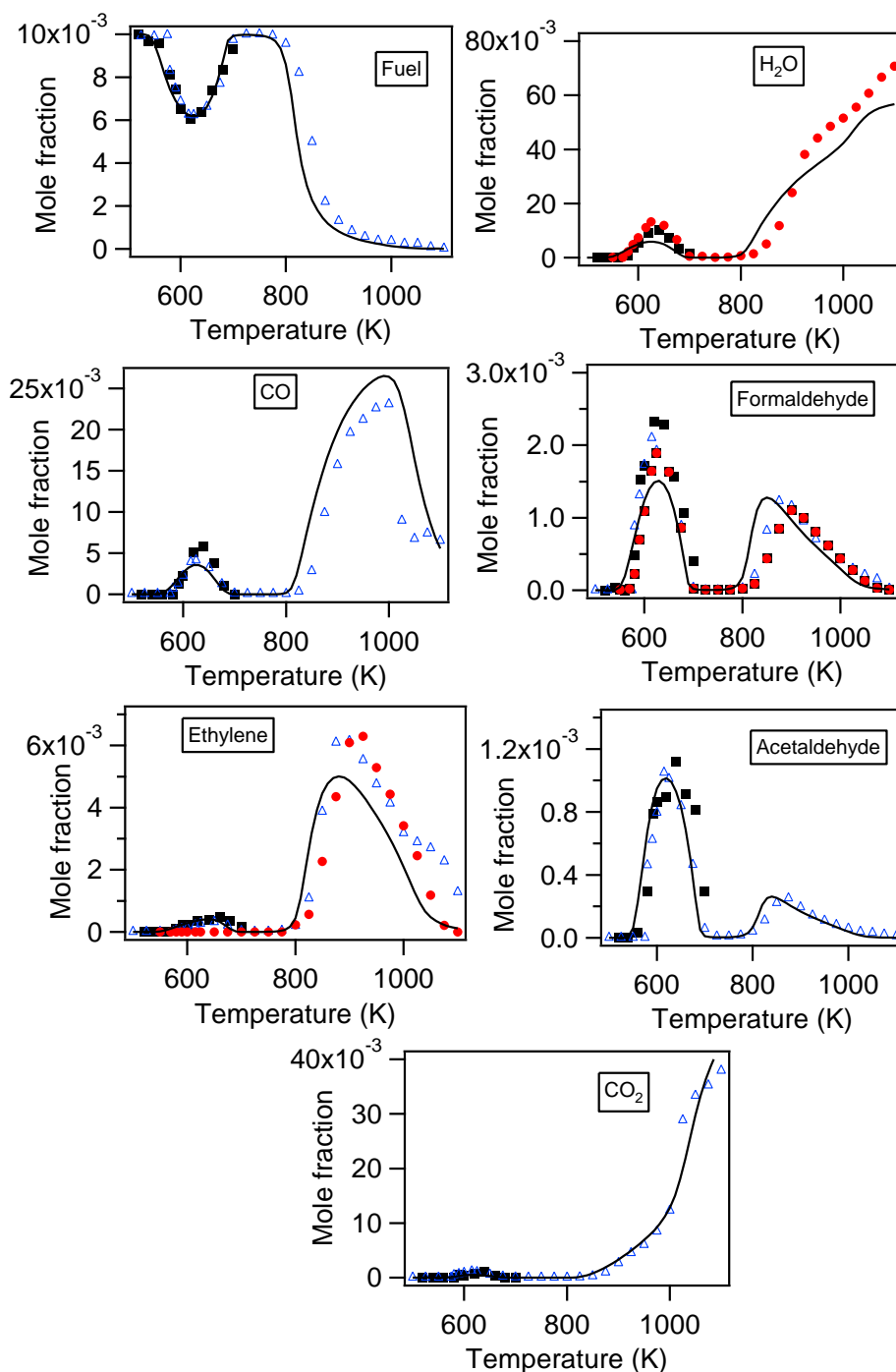


Figure S4: Temperature evolutions of the mole fractions of fuel and water, carbon oxides, ethylene and C₁-C₂ aldehydes measured by synchrotron VUV photoionization mass spectrometry (black squares) and comparison with gas-chromatographic [9] (blue triangles) or cw-CRDS (red circles) measurements. Full lines are computed using the model of [15].

3c/ Temperature evolutions of the mole fractions of the propene and acetaldehyde quantified by laser photoionization mass spectrometry – Comparisons with other analytical techniques

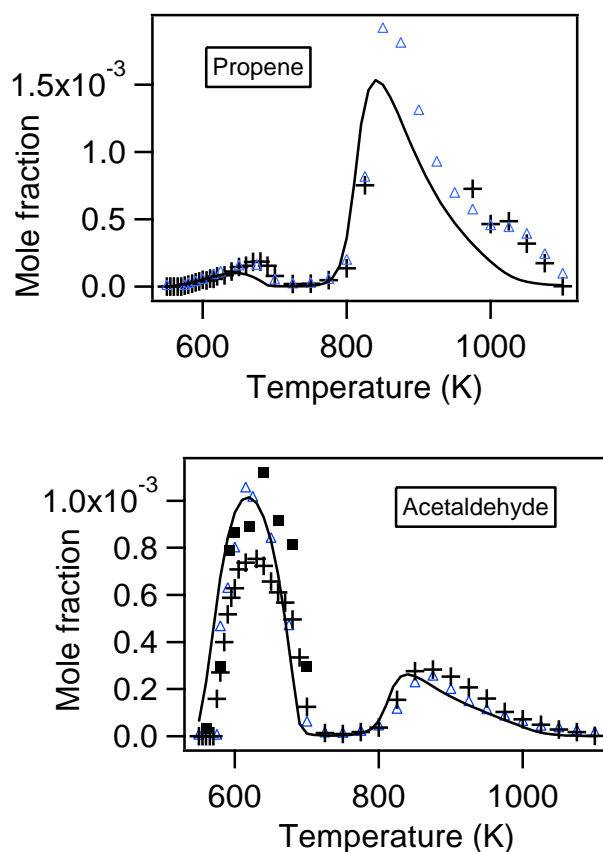


Figure S5: Temperature evolutions of the mole fractions of propene (measurements are not possible between 850 and 950 K due to an overloading of the signal) and acetaldehyde measured by laser photoionization mass spectrometry (black crosses) and comparison with gas-chromatographic [9] (blue triangles) or synchrotron VUV photoionization mass spectrometry (black squares). Lines are computed using the model of [15].

4/ Experimental photoionization efficiency spectra of hydroperoxides and diones

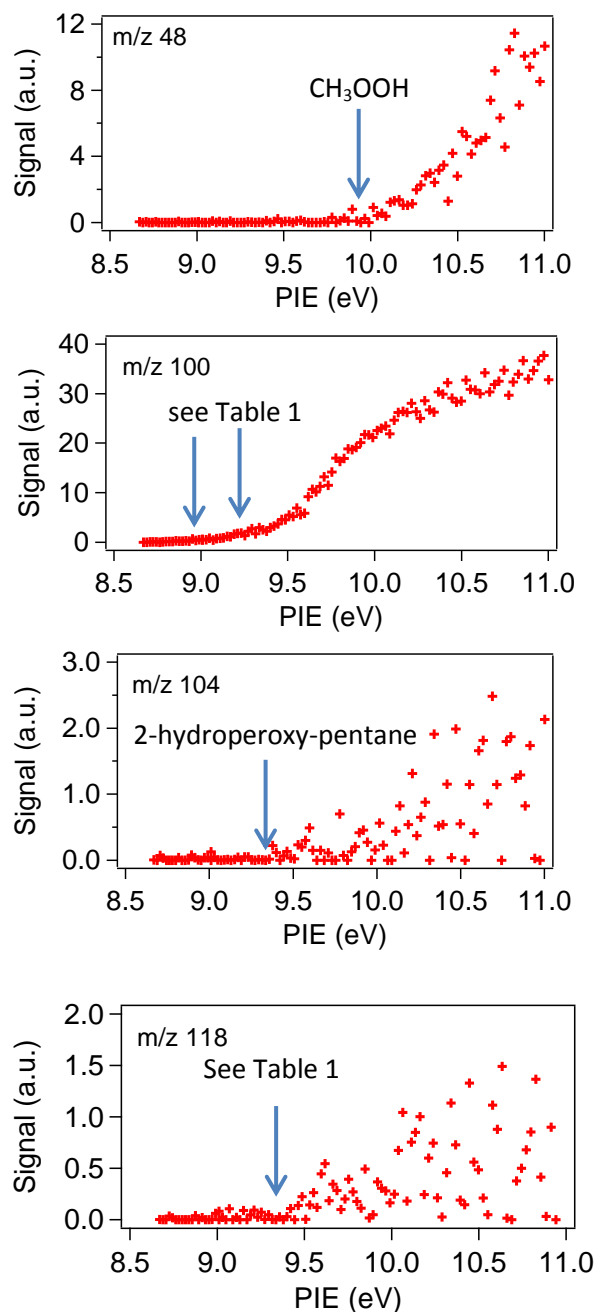


Figure S6: Photoionization efficiency spectra (PIE) at m/z 48, 100, 104, and 118. The temperature in the reactor was 630 K.

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