Hydroperoxide Measurements During Low-Temperature Gas-Phase Oxidation of *n*-Heptane and *n*-Decane

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SUPPLEMENTARY INFORMATION

1/ Gas chromatography method

Products are analyzed directly by gas chromatography using a heated transfer line between the reactor outlet and the chromatograph sampling. The temperature of the line was heated to 433 K to avoid product condensation during transfer. Three gas chromatographs were used for the quantification of the different species. The first chromatograph, equipped with a Carbosphere packed column, a thermal conductivity detector (TCD) and a flame ionization detector (FID), was used for the quantification of O_2 , CO, CO₂, methane, ethylene, acetylene and ethane. The second was fitted with a PlotQ capillary column and a FID was used for the quantification of molecules from methane to reaction products containing up to five carbon atoms and one or two oxygen atoms maximum. The FID was preceded by a methanizer (nickel catalyst for hydrogenation) which made it possible to detect species like CO, CO₂ and CH₂O with a good sensitivity. The third was fitted with a HP-5 capillary column and an FID was used for the quantification of molecules which contain at least five carbon atoms.

The identification of reaction products was performed using a gas chromatograph equipped with a PlotQ or an HP-5 capillary column and coupled to a mass spectrometer (quadrupole). The mass spectra of all of the detected reaction products were included in the NIST 08 Mass Spectra Database¹. Calibrations were performed by injecting standards where available or by using the effective carbon number method when standards were unavailable. The maximum relative error in mole fractions was estimated to be $\pm 5\%$ for species which were calibrated using standards and $\pm 10\%$ for species calibrated using the effective carbon number method^{2,3}.



Figure S1: Temperature mole fraction profiles observed for the fuel during the JSR oxidation of *n*-heptane^{4,5} for various equivalence ratios (ϕ) and of *n*-decane for two inlet mole fractions (present work) under stoichiometric conditions for a residence time of 2 s. Symbols are experiments and lines simulations.

3/ Cross-sections (σ) used for the quantification of species detected by mass

spectrometry

a/Literature cross sections

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

- 10.6 eV for laser photoionisation
- 11.0 or 13.05 eV for SVUV-photoionisation.

 O_2 (IE of 12.07 eV), and water (IE of 12.66) were only detected using SVUV-PIMS. O_2 was quantified assuming no reaction below 520 K; water was quantified using the signal of argon recorded at 16.6 eV as reference.

Table S1: Cross-sections used for the quantification of species detected by mass spectrometr	ry.
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				σ (Mb)		Deferre
Compound name	Formula	m/z	IE (eV)	at 10.6 eV	at 11.0 eV	Reference
Decenyl-OOH	$C_{10}H_{20}O_2$	172	-	20.8	35.00	Estimated*
Decane-diones	$C_{10}H_{18}O_2$	170	-	21.21	33.42	Estimated*
Nonenyl-OOH	$C_9H_{18}O_2$	158	-	20.07	32.50	$Estimated^*$
C ₇ -ketohydroperoxide	$C_7H_{14}O_3$	146	-	16.04	25.55	$Estimated^*$
Heptenyl-OOH	$C_7H_{14}O_2$	130	≈9.1	18.62	27.50	$Estimated^*$
Heptane-diones	$C_7H_{12}O_2$	128	-	19.03	25.92	$Estimated^*$
Hexenyl-OOH	$C_6H_{12}O_2$	116	≈9.2	17.89	25.00	$Estimated^*$
Pentenyl-OOH	$C_{5}H_{10}O_{2}$	102	≈9.2	17.16	22.50	$Estimated^*$
<i>n</i> -heptane	C ₇ H ₁₆	100	9.93	14.59	25.17	Zhou et al. ⁶
Heptenes	C7H14	98	-	14.27	22.41	$Estimated^*$
Butenyl-OOH	$C_4H_8O_2$	88	9.29	16.43	20.00	$Estimated^*$
Propyl-OOH	$C_3H_8O_2$	76	9.53	5.80	10.09	$Estimated^*$
Allyl-OOH	$C_3H_6O_2$	74	9.55	15.71	17.5	$Estimated^*$
Pentadienes	C ₅ H ₈	68	8.59	21.35	21.00	Yang et al. ⁷
Ethyl-OOH	$C_2H_6O_2$	62	9.61	5.07	7.59	$Estimated^*$
Propanal	C ₃ H ₆ O	58	9.96	9.94	10.77	Wang et al. ⁸
Butenes	C ₄ H ₈	56	9.55	9.85	11.10	Wang et al. ⁸
Butadienes	C ₄ H ₆	54	9.07	16.38	19.91	Yang et al. ⁷
Methyl-OOH	CH ₄ O ₂	48	9.84	4.35	5.09	$Estimated^*$
Acetaldehyde	C ₂ H ₄ O	44	10.229	8.06	7.96	Cool et al. ⁹
Propene	C ₃ H ₆	42	9.73	11.36	9.73	Cool et al. ⁹
Ketene	$\overline{C_2H_2O}$	42	9.62	22.52	15.81	Yang et al. ⁷
Formaldehyde	CH ₂ O	30	10.88	-	9.02	Cooper et al. ¹⁰
Ethylene	C_2H_4	28	10.5138	-	7.79	<i>Cool et al.</i> ¹¹

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

b Cross sections estimated using the group additivity method proposed by Bobeldijk et al.¹²



Scheme S1: Bonded atom pairs contributing in cross-section estimation in a ketohydroperoxide molecule.

Compound	IE (eV)	Reference	$\sigma_{(C\text{-}C)}$ at 10.6 eV (Mb)	$\sigma_{(C\text{-}C)}$ at 11.0 eV (Mb)
<i>n</i> -butane	10.53	Wang et al. ⁸	-	2.54
iso-butane	10.68	Yang et al. ⁷	-	2.36
<i>n</i> -pentane	10.28	Zhou et al. ⁶	0.73	4.40
Cyclohexane	9.88	Zhou et al. ¹³	4.06	7.28
Me-cyclopentane	9.70	Wang et al. ⁸	1.35	3.77
<i>n</i> -hexane	10.13	Zhou et al. ⁶	1.57	4.98
<i>n</i> -heptane	9.93	Zhou et al. ⁶	2.43	5.84
		Average	2.03	4.45
		Standard deviation	1.29	1.76
	Relative	e standard deviation	64%	40%

Table S2: Calculation of the contribution of the group C-C.

Table S3: Calcu	ulation of the	contribution	of the	group C=O.
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Compound	IE (eV)	Reference	$\sigma_{(C=O)}$ at 10.6 eV (Mb)	$\sigma_{(C=O)}~$ at 11.0 eV (Mb)
Acetaldehyde	10.22	Cool et al. ⁹	7.33	5.46
Acetone	9.70	Zhou et al. ¹³	9.56	6.33
Propanal	9.96	Wang et al. ⁸	8.49	5.77
iso-butanal	9.71	Yang et al. ⁷	8.96	5.40
<i>n</i> -butanal	9.82	Yang et al. ⁷	7.16	4.84
		Average	8.30	5.56
Standard deviation			1.03	0.55
	Relativ	e standard deviation	12%	10%

Compound	IE (eV)	Reference	$\sigma_{(C=C)}$ at 10.6 eV (Mb)	$\sigma_{(C=C)}$ at 11.0 eV (Mb)
Propene	9.73	Cool et al. ⁹	10.63	9.91
1-butene	9.55	Wang et al. ⁸	8.40	6.1
cis-2-butene	9.11	Wang et al. ⁸	10.02	9.11
trans-2-butene	9.10	Yang et al. ⁷	11.05	9.01
iso-butene	9.22	Wang et al. ⁸	9.06	6.78
1-pentene	9.49	Wang et al. ⁸	12.88	9.87
cis-2-pentene	9.01	Cool et al. ¹¹	10.73	8.98
trans-2-pentene	9.04	Cool et al. ¹¹	12.06	8.8
2-Me-2-butene	8.69	Yang et al. ⁷	13.17	10.92
3-Me-1-butene	9.52	Yang et al. ⁷	5.96	2.62
		Average	10.39	8.21
		Standard deviation	2.18	2.43
	Relativ	e standard deviation	21%	30%

Table S4: Calculation of the contribution of the group C=C.

Table S5: Calculation of the contribution of the group C-O.

Compound	IE (eV)	Reference	$\sigma_{(C\text{-}O)}$ at 10.6 eV (Mb)	$\sigma_{(C-O)}$ at 11.0 eV (Mb)
Dimethyl-ether	10.03	Cool et al. ¹¹	4.35	5.19
Ethyl-Methyl-ether	9.72	Kameta et al. ¹⁴	5.55	5.13
1-propanol	10.22	Cool et al. ¹¹	3.74	4.08
Diethyl-ether	9.51	Cool et al. ¹¹	4.92	4.22
1-butanol	9.99	Xie et al. ¹⁵	5.58	6.44
		Average	4.83	5.01
Standard deviation			0.79	0.95
Relative standard deviation			16%	19%

Considering that for this cross section estimation method is still usable for alkenyl-OOH, using these values and assuming that the unknown contribution of the group O-O is equal to that of the C-C group, an uncertainty below 50% can be assumed on the estimated cross sections of alkenyl-OOH. Below is an example calculation of the uncertainty in the estimated cross section in the case of allyl- and decenyl-OOH.

<u>at 10.6 eV</u>

 $\sigma_{C_{3}H_{5}OOH} = 1. \sigma_{C-C} + 1. \sigma_{O-O} + 1. \sigma_{C=C} + 1. \sigma_{C-O} = 19.28 \pm 5.55 \text{ a relative error of } 28.8 \%$ $\sigma_{C_{10}H_{19}OOH} = 8. \sigma_{C-C} + 1. \sigma_{O-O} + 1. \sigma_{C=C} + 1. \sigma_{C-O} = 33.48 \pm 14.58 \text{ a relative error of } 43.6 \%$ $\underline{at 11.0 \ eV}$

 $\sigma_{C_{3}H_{5}OOH} = 1. \sigma_{C-C} + 1. \sigma_{O-O} + 1. \sigma_{C=C} + 1. \sigma_{C-O} = 22.12 \pm 6.90 \text{ a relative error of } 31.2 \%$ $\sigma_{C_{10}H_{19}OOH} = 8. \sigma_{C-C} + 1. \sigma_{O-O} + 1. \sigma_{C=C} + 1. \sigma_{C-O} = 53.28 \pm 19.26 \text{ a relative error of } 36.1 \%$

4/ Description of the cw-CRDS analyses and the related quantification $method^{16}$

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 ± 13 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 mm) for mode matching so as to excite the fundamental TEM₀₀ mode. Two folding micrometric mirrors allow easy alignment of the beam, as shown in Figure S2.



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 or the ring-down time next to a sharp absorption line) and the ring-down time τ , when performing an experiment at a given temperature:

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

where σ_a 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, and c is the speed of light. Knowing the absorption cross section σ_a , one can extract the concentration [A] of the target molecule.

5/Theoretically calculated ionization energies for $C_3H_5OOCH_3$ and C_7 compounds including an alcohol and a ketone functions

Table S6: Theoretically calculated ionization energies for C3H5OOCH3 and C7 compounds including an alcohol and a ketone functions.

Molecule	3 D representation	Calculated EI (eV)
<u>C4</u> methyl-prop-1-enyl-peroxide	ئچ ∙ و في في	8.98
methyl-prop-2-enyl-peroxide	3 .	8.36
<u>C7</u>		
1-hydrox-3-heptanone	ىقوقوقوق ،	9.44
2-hydrox-4-heptanone		9.07
3-hydrox-5-heptanone		9.14
3-hydroxy-heptanal	مۇرغۇغۇغ	9.48
4-hydroxy-2-heptanone		9.28

6/Comparison between the PIE spectrum obtained at m/z 170 during n-decane oxidation (present work) and that obtained at m/z 128 during n-heptane oxidation⁵



Figure S3: Comparison between the PIE spectrum obtained at m/z 170 during n-decane oxidation (present work) and that obtained at m/z 128 during n-heptane oxidation.⁵

7/Thermochemical data under CHEMKIN format for alkenyl hydroperoxides calculated by quantum theoretical method

Species	NASA polynomial of thermochemical data				
structure					
^O OH	C3H500H C 3H 6O 2 G 300.000 5000.000 1000.00	1			
	9.16538572E+00 2.05557099E-02-8.09573596E-06 1.46868055E-09-1.00471035E-13	2			
	-1.03349208E+04-2.02569184E+01 3.30114483E+00 2.62880531E-02 9.89267971E-06	3			
	-2.82482169E-08 1.17599084E-11-8.27584157E+03 1.24658092E+01	4			
	C 4H 80 2 G 300.000 5000.000 1000.00	1			
И СОН	1.11703859E+01 2.72017275E-02-1.07274288E-05 1.94769565E-09-1.33310304E-13	2			
I	-1.59719640E+04-3.10096904E+01 3.42725713E+00 3.58145222E-02 9.89295980E-06	3			
	-3.41589505E-08 1.44832813E-11-1.33053523E+04 1.19363601E+01	4			
	C4H700H C 4H 80 2 G 300.000 5000.000 1000.00	1			
C CH	1.06677717E+01 2.78651157E-02-1.10392002E-05 2.01046958E-09-1.37899780E-13	2			
	-1.52705435E+04-2.74501282E+01 4.75447022E+00 2.67058294E-02 2.79184677E-05	3			
	-4.87738014E-08 1.87612911E-11-1.28472586E+04 7.28125653E+00	4			
$\wedge \wedge$	C5H90OH C 5H 100 2 G 300.000 5000.000 1000.00	1			
Г Тон	1.26845469E+01 3.44461651E-02-1.36322735E-05 2.48100510E-09-1.70094224E-13	2			
	-1.91100931E+04-3.84156931E+01 3.76893618E+00 4.07975650E-02 2.08071910E-05	3			
	-4.97896808E-08 2.02253380E-11-1.58614189E+04 1.19247355E+01	4			
	С5Н9ООН С 5Н 100 2 G 300.000 5000.000 1000.00	1			
/ / / ОН	1.22123586E+01 3.50765634E-02-1.39301070E-05 2.54115770E-09-1.74500991E-13	2			
	-1.83880061E+04-3.46979846E+01 4.98062437E+00 3.23423389E-02 3.76629721E-05	3			
	-6.35153900E-08 2.42549263E-11-1.53586012E+04 8.10624330E+00	4			
<u> </u>	C5H90OH C 5H 100 2 G 300.000 5000.000 1000.00	1			
	1.26848974E+01 3.44964134E-02-1.36641008E-05 2.48811468E-09-1.70638051E-13	2			
°∕ _{OH}	-2.07902867E+04-3.81355229E+01 4.97698724E+00 3.58440789E-02 2.85403634E-05	3			
011	-5.51321697E-08 2.16054268E-11-1.77745060E+04 6.42168161E+00	4			

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