Electronic Supplementary Information to:

Kinetics of the a-C_3H_5 + O_2 reaction, investigated by photoionization using synchrotron radiation.

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Figure S1: Response function used in the fit to the experimental data.

Figure S2: ms-TPES of the allyl radical, generated by photolysis of C_3H_5I

Figure S3: Kinetic trace of the *m/z* 68 ion signal

Figure S4: Experimental time/concentration profile and sensitivity analysis for allyl generated by 213 nm photolysis of allyl iodide.

Table S1: Overview of the experimental conditions

Table S2: List of bimolecular rate constants

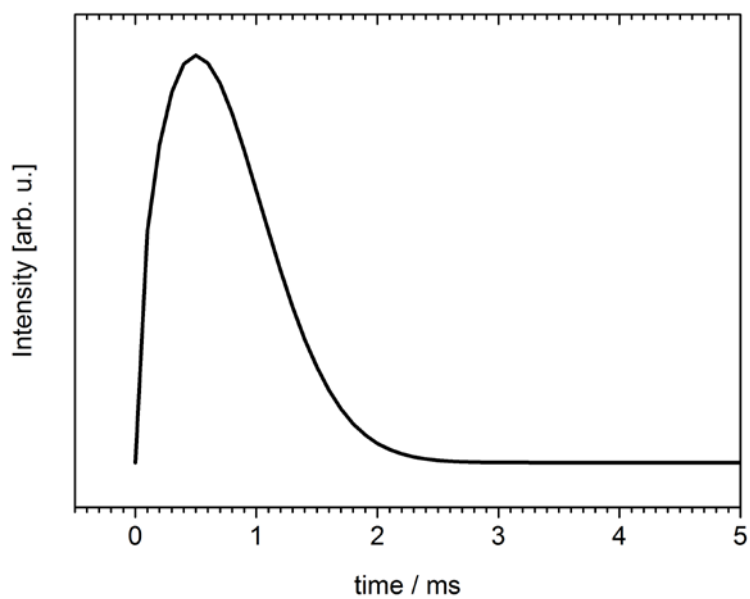**Table S3:** List of pseudo-first-order rate constants

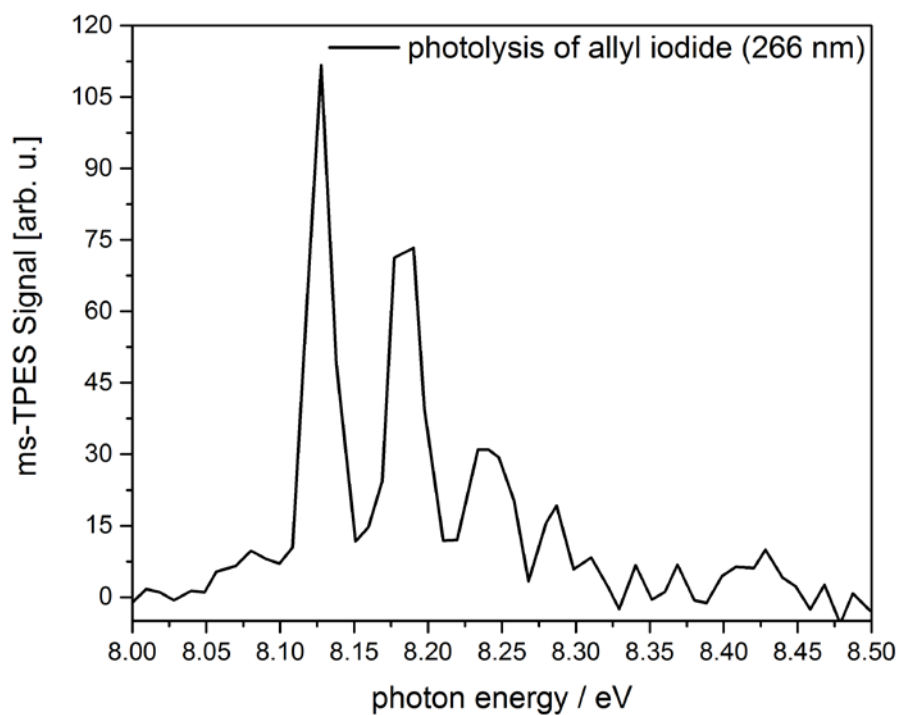**Fig. S1:** Response function used in the fit to the experimental data.

Fig. S2: ms-TPES of the allyl radical between 8.0 and 8.5 eV. Allyl radicals were generated at 0.8 mbar by photolysis of allyl iodide at 266 nm. Every point was averaged for 300 s and the resolution is 10 meV.
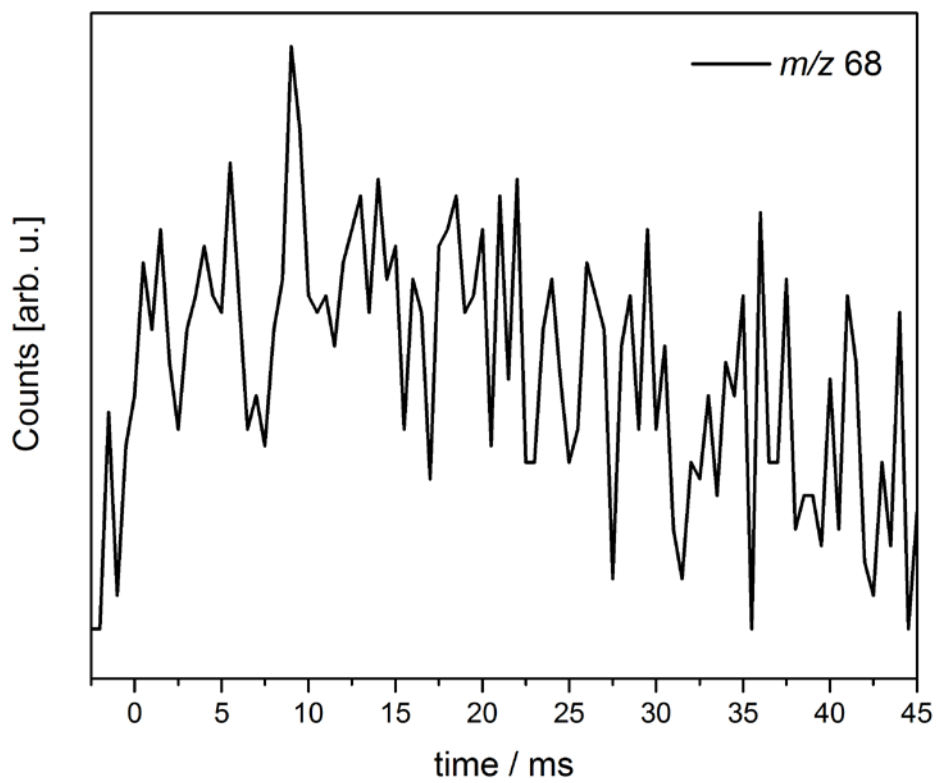
Fig. S3: Kinetic trace of the *m/z* 68 ion signal, showing that the molecule is indeed formed during the experiment.
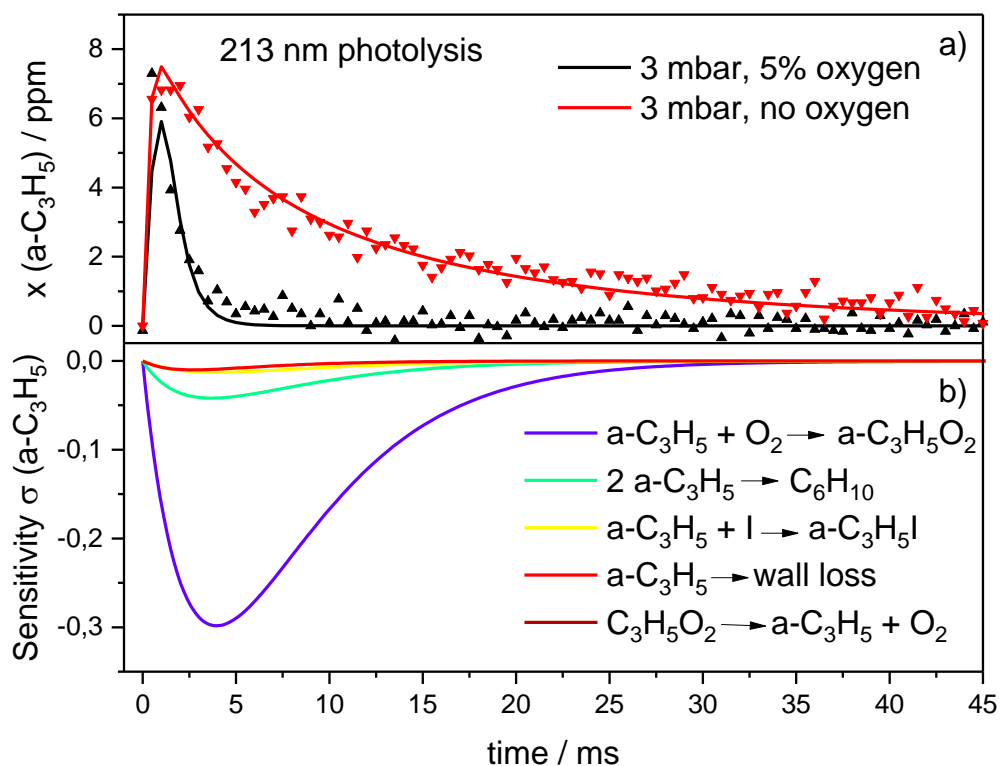
Figure S4: a) Experimental concentration-time profiles of the allyl radical generated by 213 nm photolysis of allyl iodide, with no oxygen (red) and 5% oxygen (black) added. The solid curves denote numerical simulations. b) Corresponding sensitivity analysis of the experiment. Dimerisation of allyl yielding hexadiene is more important than at 266 nm photolysis due to higher C_3H_5 concentration, but the influence of the reaction on the overall kinetics is still small compared to the reaction with oxygen.

Table S1: Overview of the experimental conditions used to measure the rate coefficient of the reaction $CH_2CHCH_2 + O_2$.

Experiment, precursor (wavelength)	[Ar]	[Precursor]$_0$	[O$_2$]	Pressure / mbar
	/ (molecule cm^{-3})			
(a) Allyl iodide (266 nm)	1.94×10^{16}	7.20×10^{12}	0	0.8
	$1.93 \times 10^{16} - 1.76 \times 10^{16}$	7.20×10^{12}	$1.94 \times 10^{14} - 1.94 \times 10^{15}$	0.8
(b) Allyl iodide (213 nm)	1.94×10^{16}	7.20×10^{12}	0	0.8
	4.86×10^{16}	1.80×10^{13}	0	2.0
	7.29×10^{16}	2.70×10^{13}	0	3.0
	$1.93 \times 10^{16} - 1.85 \times 10^{16}$	7.20×10^{12}	$9.72 \times 10^{13} - 9.72 \times 10^{14}$	0.8
	$4.83 \times 10^{16} - 4.61 \times 10^{16}$	1.80×10^{13}	$2.43 \times 10^{14} - 2.43 \times 10^{15}$	2.0
	$7.25 \times 10^{16} - 6.92 \times 10^{16}$	2.70×10^{13}	$3.65 \times 10^{14} - 3.65 \times 10^{15}$	3.0
(c) Propene (266 nm)	2.18×10^{16}	2.43×10^{14} [a] 2.19×10^{15} [b]	0	1.0
	$2.16 \times 10^{16} - 1.93 \times 10^{16}$	2.43×10^{14} [a] 2.19×10^{15} [b]	$2.43 \times 10^{14} - 2.43 \times 10^{15}$	1.0

a: propene; b: oxalyl chloride

Table S2: Bimolecular rate constants k_1 obtained from a least-square fit of the concentration-time profiles (ChemKin).

Experiment (p_R)	k_1 obtained from a least-square fit of the concentration-time profiles / 10^{11} cm³ s⁻¹ mol⁻¹					
	[O_2] = 0.5%	[O_2] = 1%	[O_2] = 3%	[O_2] = 5%	[O_2] = 7.5%	[O_2] = 10%
Ia	-	1.45	1.39	1.28	1.32	1.31
Ib (0.8 mbar)	1.42	1.41	1.40	1.39	-	-
Ib (2.0 mbar)	1.48	1.53	1.54	1.60	-	-
Ib (3.0 mbar)	1.72	1.68	1.78	1.82	-	-
II	-	1.49	1.40	1.55	1.64	1.53

Table S3: Pseudo-first-order rate constants $k^{1st} = k_1 \cdot [O_2]$ obtained in the individual experiments.

Experiment (p_R)	k^{1st} /s⁻¹					
	[O_2] = 0.5%	[O_2] = 1%	[O_2] = 3%	[O_2] = 5%	[O_2] = 7.5%	[O_2] = 10%
Ia	-	47	135	207	320	423
Ib (0.8 mbar)	23	46	136	224	-	-
Ib (2.0 mbar)	60	124	373	646	-	-
Ib (3.0 mbar)	104	203	647	1101.83	-	-
II	-	61	144	320	507	631