

Supplementary information:

Ultraviolet photochemistry dynamics of the 2-buten-2-yl radical

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1. Background removal in the H-atom TOF spectrum of 2-buten-2-yl

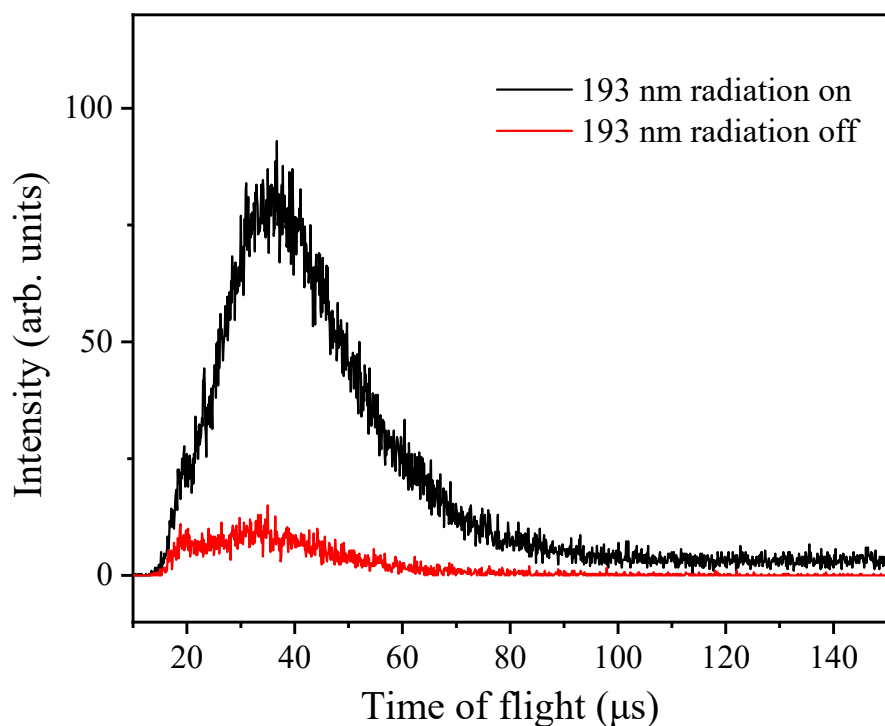


Fig. S1 Sample H-atom TOF spectra of 236-nm photodissociation of 2-buten-2-yl from 2-chloro-2-butene, with the 193-nm photolysis laser radiation on and off. The polarization vector of the 236 nm photodissociation radiation was parallel ($\theta = 0^\circ$) to the TOF axis. The red line recorded with the 193-nm photolysis laser off, represents background signals resulting from 236-nm photodissociation of the 2-chloro-2-butene precursor. By subtracting this 193-nm off spectrum from the 193-nm on spectrum, the net H-atom TOF spectrum originating from the 236-nm photodissociation of 2-buten-2-yl is obtained (as shown in Fig. 3, after accumulating over a larger number of laser shots).

2. Structure and excited electronic states of *trans*-2-buten-2-yl

Table S1. Cartesian coordinates (in Å) for the ground state structure of *trans*-2-buten-2-yl optimized using CCSD/aug-cc-pVDZ. Electronic energy is -156.088535 Hartree.

C	2.02521800	-0.03823300	-0.00000200
H	2.50981900	-0.46848300	-0.89296100
H	2.50980700	-0.46861800	0.89289900
H	2.20692500	1.05614400	0.00008200
C	0.55864700	-0.30982600	-0.00003900
C	-0.56771700	0.40146400	-0.00000100
H	-0.47883100	1.50418300	0.00011000
C	-1.97235200	-0.16869300	0.00001300
H	-2.53166400	0.16934600	0.89066600
H	-2.53173200	0.16950300	-0.89053700
H	-1.94709900	-1.27034600	-0.00008400

Table S2. Cartesian coordinates (in Å) for the D₅ excited state structure of *trans*-2-buten-2-yl optimized using EOM-CCSD/daug-cc-pVDZ. Electronic energy is -155.901421 Hartree.

C	2.01537300	-0.10277200	-0.00001900
H	2.35990600	-0.59186300	-0.92408600
H	2.35997600	-0.59193900	0.92398100
H	2.46254400	0.93625600	0.00000700
C	0.60456200	0.16361100	0.00005800
C	-0.62513500	0.53615500	0.00013500
H	-0.67947000	1.64489600	0.00014000
C	-1.94276300	-0.23590200	0.00000200
H	-2.50364200	0.06923700	0.90129800
H	-2.50358000	0.06939500	-0.90128500
H	-1.76675100	-1.32063400	-0.00008600

Table S3. Cartesian coordinates (in Å) for the D₆ excited state structure of *trans*-2-buten-2-yl optimized using EOM-CCSD/daug-cc-pVDZ. Electronic energy is -155.8978684 Hartree.

C	1.99593000	-0.11506600	0.00030600
H	2.30551600	-0.64475700	-0.91748800
H	2.30523100	-0.64374900	0.91877300
H	2.53856400	0.87355400	-0.00019000
C	0.60031300	0.23613300	-0.00010700
C	-0.65323100	0.65114100	-0.00054900
H	-0.79749400	1.74450700	-0.00097700
C	-1.89722900	-0.23601800	-0.00004900
H	-2.48940800	0.00638800	0.90090600
H	-2.49192800	0.00882700	-0.89864200
H	-1.63524200	-1.30451900	-0.00183800

Table S4. Excited state energies of *trans*-2-buten-2-yl obtained with different electronic structure methods. Vertical excitation energies (VEE) are converted into nm and the oscillator strengths (f) are provided accordingly. The ground-state molecular geometry was optimized using CCSD/aug-cc-pVDZ optimized structure. Dominant natural transition orbital (NTO) excitations of *trans*-2-buten-2-yl obtained with CAM-B3LYP/6-31++G are listed for reference.

Excited states	NTO dominant transition	CAM-B3LYP/6-31++G		CAM-B3LYP/aug-cc-pVQZ		CAM-B3LYP/daug-cc-pVQZ		EOM-CCSD/aug-cc-pVDZ	
		VEE (nm)	f	VEE (nm)	f	VEE (nm)	f	VEE (nm)	f
D ₁	$\pi \rightarrow n$	411.5	0.002	445.2	0.001	445.2	0.001	397.7	0.001
D ₂	$\pi \rightarrow \pi^*$	285.5	0.000	301.2	0.000	301.2	0.000	264.8	0.000
D ₃	$n \rightarrow \pi^*$	259.8	0.002	263.6	0.001	263.7	0.001	242.2	0.002
D ₄	$n \rightarrow 3s$ Ry	229.3	0.002	222.7	0.002	223.2	0.002	217.4	0.002
D ₅	$n \rightarrow 3p_y$ Ry	205.3	0.080	202.4	0.074	203.4	0.069	198.2	0.075
Adiabatic excitation energy of D ₅ (nm)		248.4		250.8		252.1		237.4	
D ₆	$n \rightarrow 3p_x$ Ry	204.7	0.029	201.1	0.012	201.8	0.011	195.2	0.029
Adiabatic excitation energy of D ₆ (nm)		239.7		244.4		245.7		234.5	
D ₇	$\pi \rightarrow 3s$ Ry	199.0	0.000						
D ₈	$\pi \rightarrow 3s$ Ry	195.1	0.007						
Excited states	NTO dominant transition	EOM-CCSD/daug-cc-pVDZ		EOM-CCSD/aug-cc-pVTZ		EOM-CCSD/daug-cc-pVTZ			
		VEE (nm)	f	VEE (nm)	f	VEE (nm)	f		
D ₁	$\pi \rightarrow n$	397.7	0.001	399.1	0.001	399.0	0.001		
D ₂	$\pi \rightarrow \pi^*$	264.9	0.000	264.9	0.000	264.9	0.000		
D ₃	$n \rightarrow \pi^*$	242.4	0.002	244.2	0.002	244.3	0.002		
D ₄	$n \rightarrow 3s$ Ry	218.8	0.002	213.8	0.002	214.3	0.002		
D ₅	$n \rightarrow 3p_y$ Ry	200.7	0.067	195.5	0.071	196.7	0.066		
Adiabatic excitation energy of D ₅ (nm)		240.2		236.5		237.8			
D ₆	$n \rightarrow 3p_x$ Ry	197.1	0.025	192.4	0.026	193.2	0.024		
Adiabatic excitation energy of D ₆ (nm)		235.8		232.1		233.4			

Table S5. Transition dipole moments and dominant natural transition orbital (NTO) excitations of *trans*-2-buten-2-yl obtained with CAM-B3LYP/6-31++G. The definition of the Cartesian x, y, and z vectors for the directions of transition dipole moments can be found in **Fig. S2**.

Excited states	Transition dipole moments				NTO		
	X	Y	Z	Squared	Character	Main transition(s)	Weight
D ₁	0	0	-0.167	0.028	π to n	15 β →16 β	1.96
D ₂	0.0335	0.023	0	0.002	π to π^*	16 α →17 α	1.06
					π to π^*	15 β →16 β	1.01
D ₃	0	0	-0.139	0.019	n to π^*	16 α →17 α	1.95
D ₄	-0.117	-0.038	0	0.015	n to 3s Ry	16 α →17 α	1.98
D ₅	-0.289	-0.676	-0.000	0.540	n to 3p _y Ry	16 α →17 α	1.99
D ₆	0.229	-0.378	-0.000	0.195	n to 3p _x Ry	16 α →17 α	1.98
D ₇	0	0	0.047	0.0022	π to 3s Ry	15 β →16 β	1.85
D ₈	0	0	0.211	0.0445	π to 3s Ry	16 α →17 α	1.43
					n to 3p _z Ry	15 α →18 α	0.45

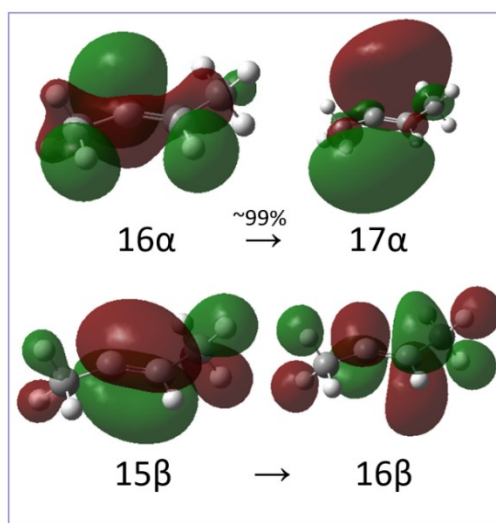
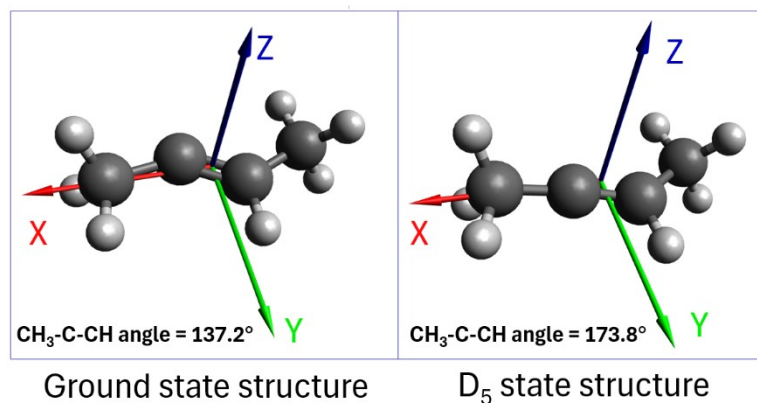


Fig. S2 The natural transition orbitals (NTOs) for transitions from the ground state D₀ to the excited state D₅ of *trans*-2-buten-2-yl (CAM-B3LYP/6-31++G). The directions of the Cartesian vectors with respect to the structures of the ground state D₀ and the D₅ state are displayed.

3. Rice–Ramsperger–Kassel–Marcus (RRKM) calculations of rate constants

The unimolecular rate constant calculations for 2-buten-2-yl decomposition into 2-butyne + H and 1,2-butadiene + H were computed using Rice–Ramsperger–Kassel–Marcus (RRKM)¹ theory under the experimental conditions. The RRKM expression for an energy dependent rate constants $k(E)$ is given

by $k(E) = \frac{\sigma W^\ddagger(E - E^\ddagger)}{h\rho(E)}$, where σ is the reaction path degeneracy, h is Planck's constant,

$W^\ddagger(E - E^\ddagger)$ is the total number of states for the transition state, and $\rho(E)$ represents the density of states of the energized reactants. The total number of states and the densities of states were determined using harmonic frequencies calculated at the CCSD(T)/aug-cc-PVTZ//CAM-B3LYP/6-311++G(d,p) level of theory. E was taken to be the excitation energy assuming it is transferred into the internal normal modes of 2-buten-2-yl. The rate constants were computed using the ab initio potential energy surface information in this work, at $p = 2 \times 10^{-6}$ Torr and $T = 298$ K, employing the MESMER package.² The calculated population of the reaction compounds over time at the 246 nm and 226 nm excitation energy are shown in Fig. S3 and S4, respectively. The rate constant for 2-buten-2-yl \rightarrow 2-butyne + H is determined to be $k = 4.5 \times 10^{11} \text{ s}^{-1}$ at 246 nm and $7.1 \times 10^{11} \text{ s}^{-1}$ at 226 nm; while for the decomposition to 1,2-butadiene + H, $k = 8.5 \times 10^{10} \text{ s}^{-1}$ at 246 nm and $1.4 \times 10^{11} \text{ s}^{-1}$ at 226 nm.

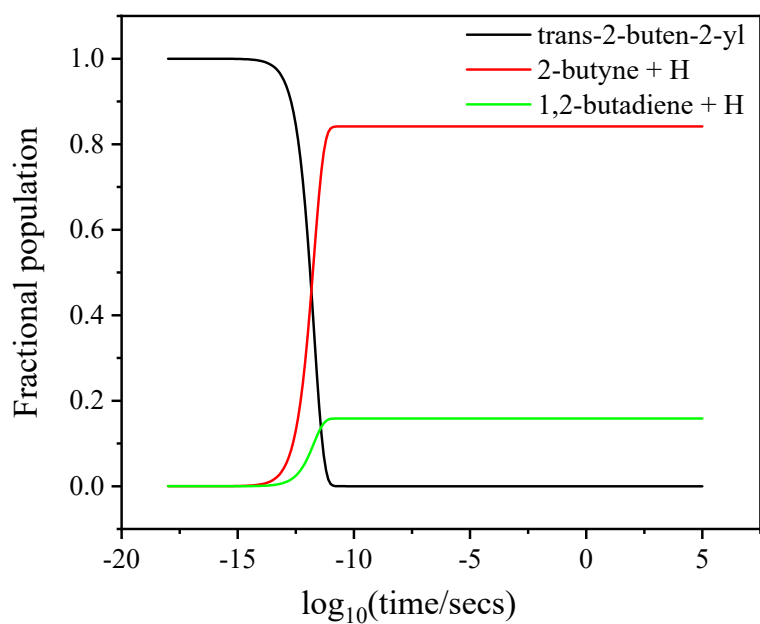


Fig. S3. The relative population for 2-buten-2-yl with an internal energy of 116.2 kcal/mol (246 nm), decomposes over time into 2-butyne + H and 1,2-butadiene + H at 298 K.

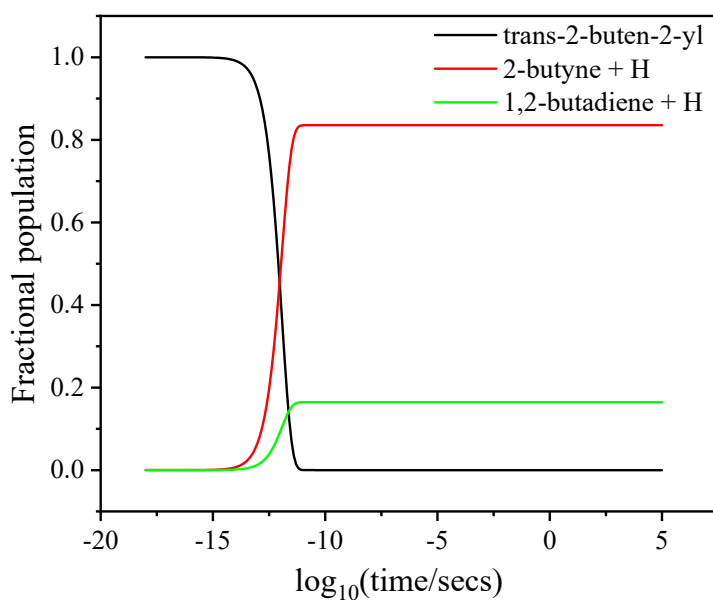


Fig. S4. The relative population for 2-buten-2-yl with an internal energy of 126.5 kcal/mol (226 nm), decomposes over time into 2-butyne + H and 1,2-butadiene + H at 298 K.

References:

1. H. Eyring, S. H. Lin and S. M. Lin, *Basic Chemical Kinetics*, John Wiley & Sons, New York, 1980.
2. D. R. Glowacki, C.-H. Liang, C. Morley, M. J. Pilling and S. H. Robertson, *J. Phys. Chem. A*, 2012, **116**, 9545-9560.