

Probing for non-statistical effects in dissociation of the 1-methylallyl radical

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1 Experimental

1.1 Synthesis of pent-3-enyl nitrite

Pent-3-enyl nitrite was prepared by the dropwise addition of H_2SO_4 (30%, 7.5 ml) to a saturated solution of NaNO_2 (3.5 g, 0.05 mol) in pent-3-en-1-ol (3.53 ml, 3 g, 0.035 mol) and water (6 ml). The reaction mixture was stirred for 90 minutes at 0 °C under a nitrogen atmosphere in the dark. The yellow product was separated with four 5 ml portions of a solution of NaCl (3 g) and sodium bicarbonate (0.4 g) in water (20 ml) to give the product (3.34 g, 0.03 mol, 85 %) as a yellow liquid.

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 5.64-5.57 (m, $\text{CH}_3\text{CH}=\text{CH}$), 5.42-5.36 (m, $\text{CH}_3\text{CH}=\text{CH}$), 4.73 (t, $\text{CH}_2\text{ON}=\text{O}$), 2.53-2.45 (m, $\text{CH}_2\text{CH}_2\text{ON}=\text{O}$), 1.64-1.61 (m, CH_3).

1.2 Synthesis of 1-iodobut-2-ene

To an efficiently stirred solution of NaI (1.5 g, 10 mmol) in CH₃CN (15 ml), Me₃SiCl (1.25 ml, 10 mmol), water (0.09 ml, 5 mmol), and crotyl alcohol (720 mg, 0.85 ml, 10 mmol) were added slowly. The reaction was allowed to react at room temperature for 30 minutes. After quenching with water (10 ml), the product was extracted with Et₂O (3 x 15 ml). The ether layer was washed with a Na₂S₂O₃ solution (15 ml, 10 %) and dried over MgSO₄. The mixture was frozen to -45 °C and the solid CH₃CN was removed. After column chromatography pure 1-Iodobut-2-ene (1.6 g, 8.6 mmol, 86 %) was obtained.

¹H-NMR (300 MHz, CDCl₃) δ 5.72 (m, CH=CH), 3.85 (m, CH₂), 1.69 (s, CH₃).

2 Computational

We calculated the geometries and energetics of the (*E*)- and (*Z*)-1-methylallyl radicals in their ground and first electronically excited states at the MCSCF(3,3)/DZP++ level of theory using the MOLPRO package.[1] The active space included the highest doubly occupied orbital (HOMO), the singly occupied orbital (SOMO) and the lowest unoccupied π^* -orbital (LUMO). We used the DZP++ basis from Dunning and Hay.[2] Figure S1 shows the calculated equilibrium geometries for both the ground and first electronically excited state. While the ground state has a planar geometry for both isomers, the first valence excited state structures are twisted around the central C–C bond resulting in out-of-plane distortions with a CCCC dihedral angle of 50.3° for the *E*-isomer and 11.6° for the *Z*-isomer.

2.1 Structures, energies and vibrational frequencies of the 1-methylallyl radical

In this section, we list the optimized cartesian coordinates, energies and vibrational frequencies obtained at the MCSCF/DZP++ level of theory for both the (*E*)-1-methylallyl and the (*Z*)-1-methylallyl radical in both the ground and first electronically excited state with valence character. We also display the structures of the transition states for isomerization and C–H bond fission based on the coordinates from Miller[3] in Fig. S2 and S3.

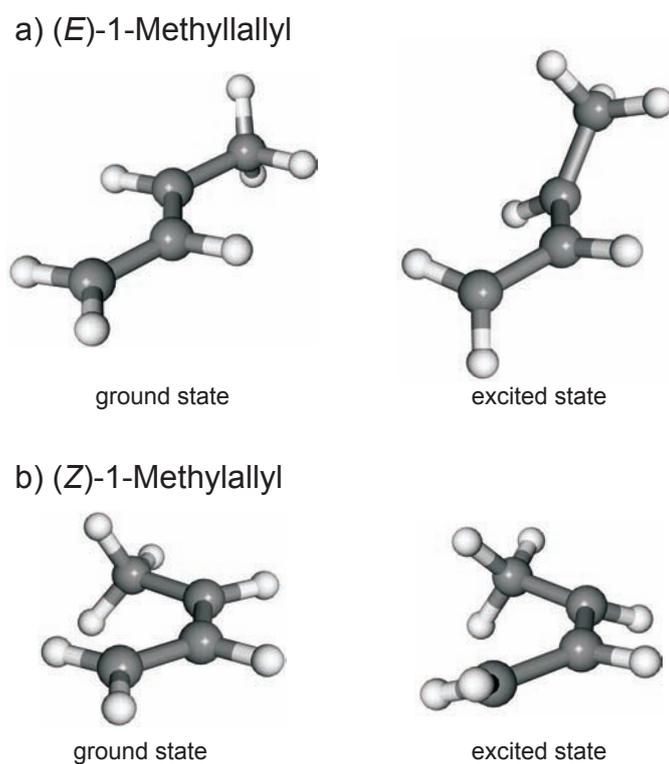


Figure S1: Optimized minimum energy structures calculated at the MCSCF/DZP++ level of theory for both the planar ground and non-planar first electronically excited state of (a) the (*E*)-1-methylallyl radical and (b) the (*Z*)-1-methylallyl radical.

Table S1: Cartesian coordinates and energy of (*E*)-1-methylallyl in the ground state obtained at the MCSCF/DZP++ level of theory.

<i>(E)</i> -1-methylallyl			
Ground state:	Energy:	-155.5556392 hartree	
	x	y	z
C	0.116449	-0.142830	0.098412
C	-0.016660	-0.046025	1.485720
C	1.279657	0.154898	-0.609999
C	1.409853	0.046428	-2.103824
H	2.195381	-0.654586	-2.377596
H	0.484023	-0.292579	-2.557626
H	1.668626	1.006936	-2.544150
H	-0.942822	-0.290884	1.972641
H	0.804431	0.275885	2.102667
H	-0.744274	-0.472213	-0.464389
H	2.146763	0.484971	-0.059515

Table S2: Cartesian coordinates and energy of (*E*)-1-methylallyl in the first excited state obtained at the MCSCF/DZP++ level of theory.

<i>(E)</i> -1-methylallyl			
Excited state:	Energy:	-155.44499522 hartree	
	x	y	z
C	0.103641	-0.137115	1.579365
C	0.085822	-0.344487	0.128373
C	1.119172	0.216683	-0.752527
C	1.822517	-0.660293	-1.753428
H	2.549492	-1.316725	-1.273754
H	1.112157	-1.294079	-2.278565
H	2.352767	-0.062364	-2.488320
H	-0.782404	0.201805	2.090080
H	1.044892	-0.019509	2.087890
H	-0.701742	-0.938322	-0.307324
H	1.631904	1.099957	-0.406417

Table S3: Cartesian coordinates and energy of (*Z*)-1-methylallyl in the ground state obtained at the MCSCF/DZP++ level of theory.

(Z)-1-Methylallyl			
Ground state:	Energy:	-155.5541793 hartree	
	x	y	z
C	-1.538630	-0.577421	0.012473
C	-0.800936	0.603616	0.000282
C	0.597102	0.698034	0.003149
C	1.530632	-0.485054	0.011877
H	1.286792	-1.180360	0.810672
H	1.483426	-1.034176	-0.926422
H	2.556379	-0.163271	0.154190
H	-2.613201	-0.552886	0.010165
H	-1.065876	-1.543013	0.022727
H	-1.351044	1.531326	-0.013534
H	1.032562	1.681712	-0.026307

Table S4: Cartesian coordinates and energy of (*Z*)-1-methylallyl in the first excited state obtained at the MCSCF/DZP++ level of theory.

(Z)-1-methylallyl			
Excited state:	Energy:	-155.443955 hartree	
	x	y	z
C	-0.81738	0.653245	-0.05468
C	-1.55997	-0.56809	0.281234
C	0.651403	0.741944	-0.14453
C	1.518375	-0.48415	-0.14671
H	1.594035	-0.9327	0.845002
H	1.120079	-1.24348	-0.81506
H	2.525237	-0.23913	-0.46925
H	-2.50783	-0.76458	-0.18733
H	-1.08414	-1.37469	0.807789
H	-1.38307	1.549494	-0.24418
H	1.098369	1.672285	0.167381

Table S5: Vibrational frequencies (in wave numbers) of the ground and first excited state structures of the (*Z*)- and (*E*)-1-methylallyl radical obtained at the MCSCF/DZP++ level of theory.

Mode	(<i>Z</i>)-Isomer		(<i>E</i>)-Isomer	
	Ground state	Excited state	Ground state	Excited state
1	26.89	117.99	126.64	88.67
2	272.49	199.01	218.23	170.27
3	320.92	245.01	302.79	272.95
4	540.42	363.95	526.84	425.09
5	605.68	381.03	554.06	450.01
6	621.27	459.72	689.69	507.48
7	720.4	564.52	708.79	532.95
8	939.41	657.09	928.75	751.66
9	986.53	900.66	1001.66	926.13
10	1079.75	1048.5	1060.49	1037.47
11	1095.81	1070.99	1097.41	1088.71
12	1156.8	1110.75	1177.7	1161.68
13	1235.68	1227.25	1222.62	1222.01
14	1266.74	1353.19	1350.18	1352.78
15	1509.11	1479.29	1438.4	1400.11
16	1526.94	1545.72	1541.18	1533.56
17	1565.21	1571.38	1587.04	1570.02
18	1607.64	1598.36	1598.48	1598.1
19	1610.67	1613.54	1617.18	1606.98
20	1639.34	1808.32	1624.67	1816.42
21	3182.03	3156.46	3177.28	3159.57
22	3238.87	3222.45	3231.32	3223.7
23	3271.13	3263.6	3264.57	3260.46
24	3325.39	3323.99	3315.12	3301.94
25	3332.96	3326.85	3326.38	3330.56
26	3362.46	3355.75	3331.73	3335.98
27	3427.31	3429.38	3423.38	3405.34

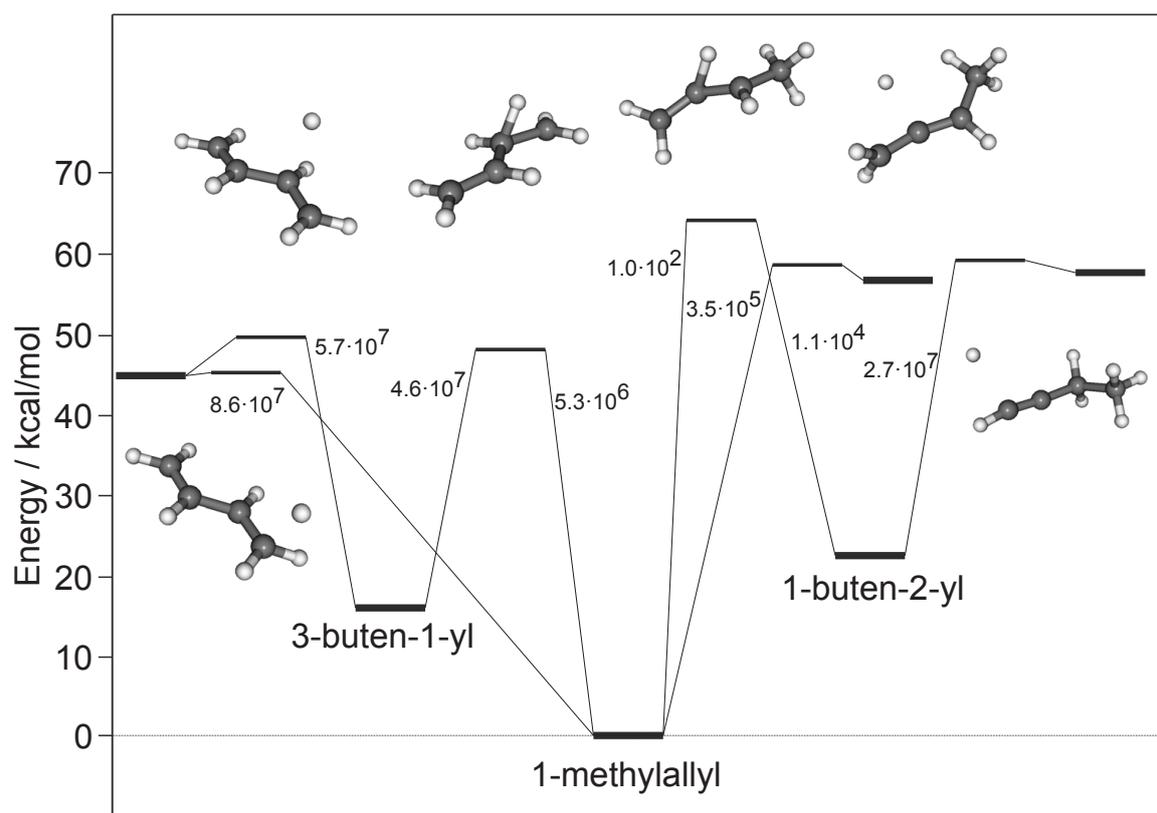


Figure S2: Structures of the transitions states for the *E*-isomers on the ground state potential energy surface for the $C_4H_7 \rightarrow C_4H_6 + H$ reaction.[3] The calculated RRKM rates for the forward and reverse reactions are also indicated in units of s^{-1} (see text for details).

3 RRKM calculations

We used the unscaled harmonic vibrational frequencies from Miller[3] for the RRKM calculations. The methyl rotors were treated as a quantized rotation with a rotation moment of inertia of $1.5 \text{ amu} \cdot \text{\AA}^2$ in the DENSUM program of the MultiWell Program Suite.[4, 5] The RRKM rates for dissociation of the *Z*-isomer to 1,3-butadiene + H is $5.80 \times 10^7 \text{ s}^{-1}$ and for the *E*-isomer $8.60 \times 10^7 \text{ s}^{-1}$. The calculated forward and reverse RRKM rate constants for the other isomerization and dissociation channels appear in Fig. S2 for the *E*-isomers and in Fig. S3 for the *Z*-isomers.

Preliminary modeling using a master equation approach[4, 5] of all isomerization and dissociation pathways appearing in Fig. S2 or Fig. S3 reveals that dissociation of 1-methylallyl produces >99% 1,3-butadiene + H. The lowest energy direct pathway for dissociation dominates with only ~6% of the photoproducts being produced by isomerization of 1-methylallyl to 3-buten-1-yl followed by C–H bond fission. Should unexpectedly 3-buten-1-yl be populated initially in the ground electronic state following non-radiative decay of C_4H_7 , this

isomer would also dissociate almost exclusively ($\sim 99\%$) to 1,3-butadiene + H. Our modeling also predicts that should 1-buten-2-yl be populated initially in the ground electronic state following non-radiative decay, this isomer of C_4H_7 would dissociate preferentially ($\sim 93\%$) to 1-butyne + H. The experimental Doppler profiles shown in Fig. S4 obtained from par-

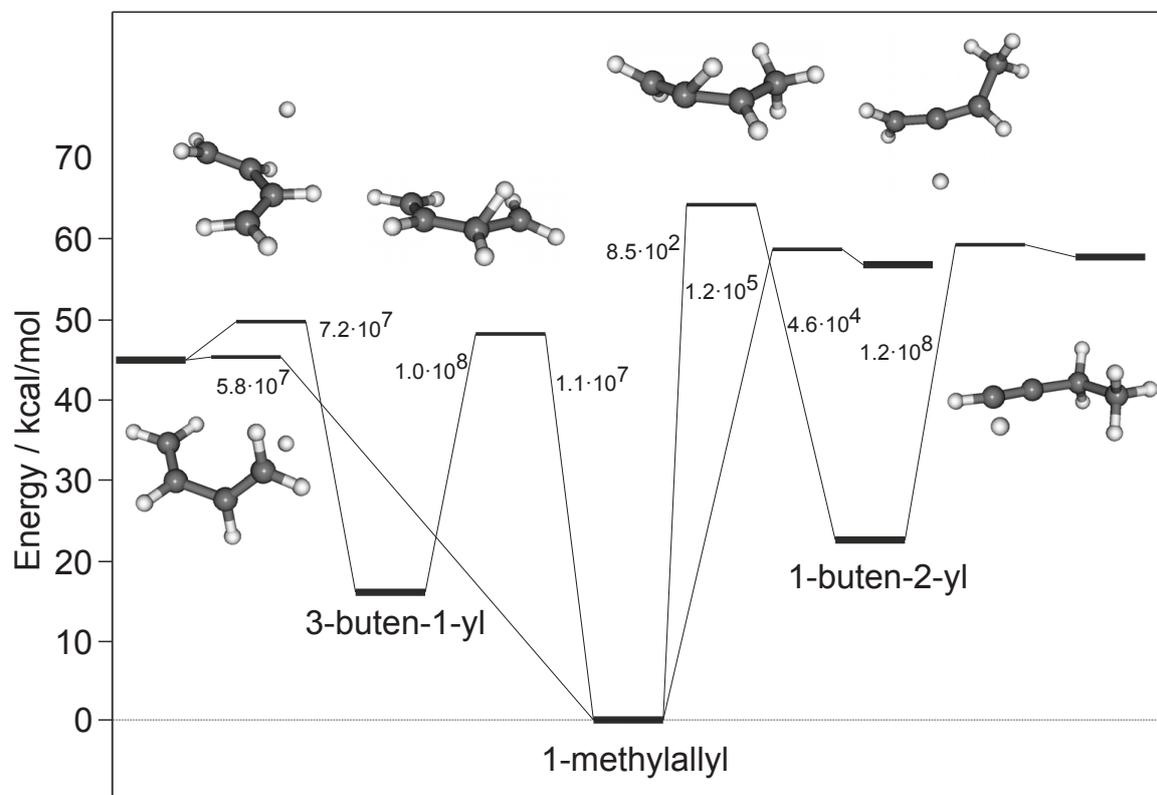


Figure S3: Structures of the transitions states for the *Z*-isomers on the ground state potential energy surface for the $C_4H_7 \rightarrow C_4H_6 + H$ reaction.[3] The calculated RRKM rates for the forward and reverse reactions are also indicated in units of s^{-1} (see text for details).

tially deuterated 1-methylallyl radicals ($CH_3CDCDCD_2$), however, reveal almost exclusive loss of hydrogen atoms, which is consistent only with 1,3-butadiene + H being the principle photoproducts in hydrogen abstraction from 1-methylallyl (see below).

4 Doppler profiles from d_4 -1-methylallyl

Figure S4 shows the Doppler profiles obtained from d_4 -1-methylallyl ($CH_3CDCDCD_2$) revealing that this radical loses almost exclusively H-atoms. The most favorable dissociation pathways for hot ground state d_4 -1-methylallyl is C-H bond cleavage in the methyl rotor to form 1,3-butadiene + H according to our RRKM modeling (see above). The small amount of deuterium observed is consistent with the minor dissociation pathway identified in our RRKM calculations to 1,3-butadiene + D that arises from an 1,2-H-shift to 3-buten-1-yl

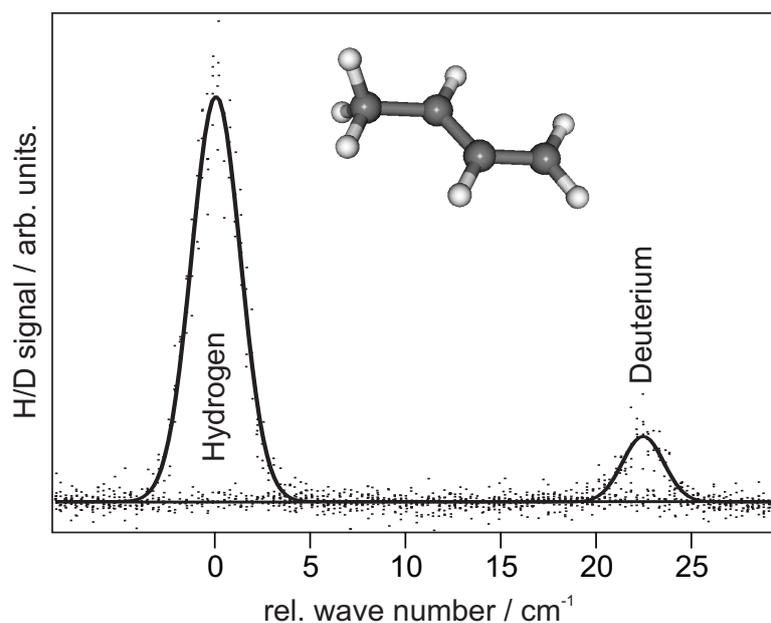


Figure S4: Doppler profiles obtained from d_4 -1-methylallyl ($\text{CH}_3\text{CDCDCD}_2$) revealing that this radical loses almost exclusively H-atoms from the methyl rotor.

followed exclusively by C–D bond fission. Should unexpectedly either d_4 -3-buten-1-yl or d_4 -1-buten-2-yl be populated following non-radiative decay to the ground state, both of these radicals would cleave only a C–D bond yielding exclusively deuterium. As we mainly observe hydrogen atoms, the dominant C–H bond fission process must be dissociation of 1-methylallyl to 1,3-butadiene + H.

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