SUPPORTING INFORMATION
Experimental Evidence for Heavy-Atom Tunneling in the Ring-Opening of Cyclopropylcarbinyl Radical from Intramolecular ^{12}C/^{13}C Kinetic Isotope Effects

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A. Experimental Procedures.

General. Oven-dried or flame-dried glassware was cooled under a stream of nitrogen prior to use, and standard syringe-and-septa techniques were employed in all cases. The reaction apparatus was a 100 mL three-necked round-bottomed flask equipped with an internal thermometer and a Vigreaux column connected to a distillation apparatus and Schlenck receiver flask (cooled in a -42 °C bath during the distillation). The system was purged with nitrogen prior to use.

**Formation and distillation of 1-butene from the ring-opening of cyclopropylcarbinyl radical, Example Procedure.** To 5 mL (44 mmol) of 1,2-dichlorobenzene at 22 °C was added 0.97 mL (1.35 g, 10 mmol) of (bromomethyl)cyclopropane by syringe. While stirring the solution, 0.2 mL (0.14 g, 1.4 mmol) of triethylborane was added dropwise to the reaction mixture. Using a syringe pump, 3.25 mL (3.52 g, 12 mmol) of tributyltin hydride was added to the solution over a 1-h period. In order to initiate the reaction, 60 mL of air was bubbled into the solution using a syringe pump over a 1-h period. Until the reaction was complete, the addition of several air bubbles at once led to an increase in the internal reaction temperature, and this temperature change was used to judge whether the reaction was complete. In addition, 0.5 mL aliquots of the reaction mixture were analyzed directly by ^{1}H NMR (applicable only to reactions at or above ambient temperature). The reactions at 22 °C were judged to be complete after the 1-h period. The reaction mixture was then distilled to afford the 1-butene. Deuterated chloroform (approximately 0.5 mL) was then added to the 1-butene and the resulting mixture was sealed in an NMR tube.

Closely analogous processes and reagent amounts were employed in procedures at 80 °C, 0 °C, -78 °C and -100 °C and in replicate procedures. For reactions performed at -78 °C and -100 °C, 5 mL (39 mmol) of methylcyclohexane was used as the solvent in place of the 1,2-dichlorobenzene that was used in the higher temperature reactions. Longer reaction times (2-3 h) were employed for the reactions at -78 °C and -100 °C.

NMR Measurements. All NMR samples were prepared in 5 mm NMR tubes filled to a constant height of 5 cm with CDCl$_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, 160 s delays between calibrated π/2 pulses, and a 5 s acquisition time to collect 347 224 points. Integrations were numerically determined using a constant integration region for each peak that was a constant

multiple of the peak widths at half height. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction is ever applied. Six spectra were recorded for each sample. The complete results from the NMR measurements and the details of the calculation of the ^{13}C ratios and KIEs are given in the next section.

NMR Integration Results. All integrations are relative integrations of C3 versus an integration of 1000 for C4. A complication in the numerical interpretation of these integrations is that C4 is subject to one ^{1}J ^{13}C-^{13}C coupling with satellites not included in the integration range, while C3 is subject to two such satellite couplings. To allow for this, the integrations at C3 were adjusted by the 0.0107(8) natural abundance of ^{13}C (*Si*). The 95% confidence ranges were calculated in a standard way. (See: http://www.iupac.org/publications/analytical_compendium/Cha02sec3.pdf.)
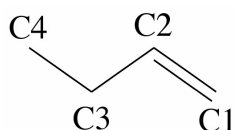
Integrations for 80 ℃

| 1047.42 | 1048.24 | 1047.53 | 1044.53 | 1051.33 | 1045.65 |
| 1055.43 | 1052.93 | 1055.96 | 1052.63 | 1056.07 | 1054.88 |

AVE   KIE
1051.05   **1.062**
Corrected   95%
1062.296   Confidence
                  0.003

Integrations for 22 ℃

| 1075 | 1067.68 | 1060.93 | 1064.25 | 1067.98 | 1065.11 |
| 1069.9 | 1066.61 | 1068.6 | 1069.85 | 1066.12 | 1066.99 |

AVE   KIE
1067.418   **1.079**
Corrected   95%
1078.84   Confidence
                  0.002

Integrations for 0 ℃

| 1075.16 | 1071.96 | 1072.3 | 1073.46 | 1064.93 | 1067.01 |
| 1068.85 | 1083.04 | 1073.49 | 1076.76 | 1079.98 | 1076.32 |

AVE   KIE
1073.605   **1.085**
Corrected   95%
1085.093   Confidence
                  0.003

Integrations for -78 ℃

1120.3	1118.94	1117.41	1119.76	1119.3	1121.94
1115.68	1121.18	1118.49	1118.42	1111.12	1111.7
1124.06	1117.04	1122.54	1119.06	1123.65	1124.63

AVE   KIE
1119.179   **1.131**
Corrected   95%
1131.154   Confidence
               0.002

Integrations for -100 ℃

1146.83	1150.08	1156.91	1152.91	1150.61	1147.89

AVE   KIE
1150.872   **1.163**
Corrected   95%
1163.186   Confidence
               0.004

B. Technical Comments

Notes on the irreversibility of the ring-opening of cyclopropylcarbinyl radical. The experimental rate constant of the reversible process (k_r) is 4.9 x 10^3 s^{-1} at 25 °C *(Sii)*. The competing rate constant of the hydrogen abstraction from the tributyltin hydride (k_H) is known to be 2.4 x 10^6 M^{-1} s^{-1} at 25 °C from the literature *(Siii)*. Although the tributyltin hydride is added slowly as a precaution, the oxygen-initiation of the reaction occurred with the tributyltin hydride concentration at 1.3 M, making the pseudo-first order rate constant of k_H 3.1 x 10^6 s^{-1} at 25 °C, 1000 times faster than k_r.

    If there were any significant reversibility of the ring opening, then the isotope effect observed would start to reflect the step transferring a hydrogen from the tin hydride to the butenyl radical. The predicted carbon isotope effect for this step at 25 °C is 1.032. Because the observed isotope effects are much higher, and agree with predictions for the ring-opening step but not the hydrogen transfer step, this weighs against significant reversibility in the reaction.

C. Calculational Procedures

Gaussrate Input File (.dat)

*General

 TITLE
methylcyclopropyl ring opening
calculation of the CVT and SCT
Information about stationary points included in the
fu5 input file

END

ATOMS
1   C
2   C
3   C
4   C
5   H
6   H
7   H

Left column:

```
  8        H
  9        H
 10        H
 11        H
END

NOSUPERMOL


INPUNIT AU

*OPTIMIZATION

 OPTMIN  OHOOK
 OPTTS  OHOOK

*SECOND

 HESSCAL HHOOK

*REACT1

 STATUS   2

# Geometry in a.u.
 GEOM
  1     2.98068545     0.00030090    -0.31999608
  2     0.51335696    -0.00013717     0.90396442
  3    -1.73107474    -1.41326461    -0.26397892
  4    -1.73108002     1.41319687    -0.26323248
  5     3.13468301     0.00180321    -2.36639373
  6     4.71080531    -0.00228637     0.77591847
  7     0.55410135    -0.00079480     2.95937608
  8    -2.99673029    -2.40331464     1.01569070
  9    -1.39258524    -2.38818004    -2.03943899
 10    -2.99676175     2.40227971     1.01719114
 11    -1.39319307     2.38934998    -2.03813886
END

ELEC
  2  0.0
END

 SPECIES   NONLINRP

*PROD1

 STATUS   2

# Geometry in a.u.
 GEOM
  1     3.38485810    -0.08325268    -0.50964307
  2     1.23486247    -0.35460982     0.77536320
  3    -1.18799482     1.05232388     0.23154238
  4    -3.34055839    -0.65902742    -0.43031897
  5     3.54365484     1.23059104    -2.08440191
```

Right column:

```
  6     5.07134811    -1.15619095    -0.03795250
  7     1.14922776    -1.70200656     2.33259882
  8    -5.27242608    -0.17187123     0.05658396
  9    -3.03245808    -2.28899271    -1.63726142
 10    -1.71105599     2.20229613     1.88369163
 11    -0.83380500     2.41681447    -1.31034403
END

ELEC
  2  0.0
END

 SPECIES   NONLINRP

*START

 STATUS   2

# Geometry in a.u.
 GEOM
  1     3.05242727    -0.08674629    -0.20729437
  2     0.72976208     0.06206769     0.98778592
  3    -1.55063561     1.36837263    -0.05359849
  4    -2.19557927    -1.28867257    -0.66394324
  5     3.35785936     0.74399342    -2.06060182
  6     4.60205034    -1.14990654     0.61280673
  7     0.56175666    -0.64528634     2.90904986
  8    -3.30968004    -2.43071196     0.62000218
  9    -1.71198495    -2.07648107    -2.48868394
 10    -2.75514567     2.31226156     1.32974745
 11    -1.17319733     2.59099997    -1.67185311
END

ELEC
  2  0.0
END

 SPECIES   NONLINTS

# end of start section

*PATH

 SCALEMASS 1.00

 RODS
 INTMU  3
 SSTEP  0.001
 INH    10

 SRANGE
  SLP  1.25
  SLM  -1.25
 END

 RPM      pagem
```

SIGN   REACTANT

IDIRECT   1

COORD curv3

INTDEF
 2-4 1-2-4 2-4-3 1-2-4-3 4-2-3
 2-1 3-2 4-3 5-1 6-1 7-2 8-4
 9-4 10-3 11-3 3-2-1 4-3-2 5-1-2 6-1-2
 7-2-3 8-4-3 9-4-3 10-3-2 11-3-2 4-3-2-1 5-1-2-3
 6-1-2-3 7-2-3-4 8-4-3-2 9-4-3-2 10-3-2-1 11-3-2-1
 END

 PRPATH
  COORD 2 4
  INTERVAL 1
  XMOL
 END

 EXFIRST
  EXPROD
  EXNSTEP 200
  EXSTEP 0.005
 END

 EXSECOND
  EXREACT
  EXNSTEP 200
  EXSTEP 0.005
 END

 SPECSTOP
  CURVE vag
  POINT savegrid
  PERCENTDOWN 95.
 END

*TUNNEL

 QUAD
  NQE 30
  NQTH 30
 END

  SCT

*RATE

**FORWARDK**

SIGMAF   1
CVT

TEMP
 100.
 102.
 104.
 110.
 120.
 123.
 125.
 127.
 130.
 140.
 148.
 150.
 152.
 160.
 170.
 173.
 175.
 177.
 180.
 190.
 200.
 202.
 210.
 220.
 223.
 225.
 227.
 230.
 240.
 248.
 250.
 252.
 260.
 270.
 280.
 290.
 296.
 298.
 300.
END

D. Gaussrate Calculated Rates.

Calculated rates for the ring-opening of cyclopropylcarbinyl radical **1** to the 3-butenyl radical **2**. Rates of a ^{13}C at position C3 and C4 are shown for CVT and CVT+SCT at temperatures ranging from 100 to 353 K.
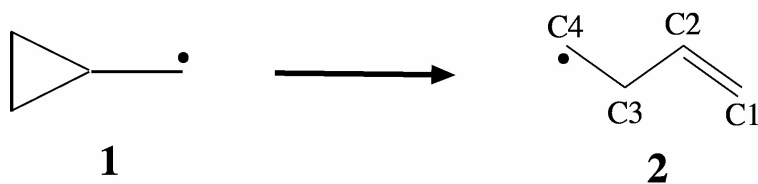
	CVT		CVT+SCT	
Temp (K)	^{13}C at C3	^{13}C at C4	^{13}C at C3	^{13}C at C4
100	3.9876E-05	3.3235E-05	1.4196E-01	2.3170E-01
102	8.5898E-05	7.1861E-05	1.7097E-01	2.7719E-01
104	1.7968E-04	1.5086E-04	2.0867E-01	3.3552E-01
110	1.4008E-03	1.1879E-03	4.0959E-01	6.3709E-01
120	2.7257E-02	2.3450E-02	1.5511E+00	2.2473E+00
123	6.0465E-02	5.2221E-02	2.3917E+00	3.3913E+00
125	1.0069E-01	8.7180E-02	3.2077E+00	4.4857E+00
127	1.6503E-01	1.4322E-01	4.3131E+00	5.9516E+00
130	3.3656E-01	2.9310E-01	6.7423E+00	9.1302E+00
140	2.9066E+00	2.5579E+00	2.9575E+01	3.8016E+01
148	1.3236E+01	1.1734E+01	9.2117E+01	1.1478E+02
150	1.8856E+01	1.6745E+01	1.2124E+02	1.5007E+02
152	2.6613E+01	2.3674E+01	1.5893E+02	1.9550E+02
170	4.1155E+02	3.7098E+02	1.4991E+03	1.7676E+03
173	7.9733E+02	7.2103E+02	2.6315E+03	3.0761E+03
180	1.4894E+03	1.3509E+03	4.5055E+03	5.2263E+03
195	8.0210E+03	7.3347E+03	1.9696E+04	2.2419E+04
200	1.3298E+04	1.2190E+04	3.0876E+04	3.4960E+04
202	1.6166E+04	1.4833E+04	3.6759E+04	4.1539E+04
210	3.4028E+04	3.1333E+04	7.1709E+04	8.0446E+04
220	8.0011E+04	7.3977E+04	1.5553E+05	1.7310E+05
223	1.0189E+05	9.4311E+04	1.9382E+05	2.1525E+05
225	1.1928E+05	1.1049E+05	2.2378E+05	2.4818E+05
227	1.3925E+05	1.2909E+05	2.5779E+05	2.8550E+05
230	1.7479E+05	1.6221E+05	3.1739E+05	3.5083E+05
240	3.5802E+05	3.3339E+05	6.1345E+05	6.7398E+05
248	6.0977E+05	5.6926E+05	1.0033E+06	1.0975E+06
250	6.9294E+05	6.4730E+05	1.1295E+06	1.2343E+06
252	7.8588E+05	7.3455E+05	1.2693E+06	1.3857E+06
260	1.2756E+06	1.1950E+06	1.9909E+06	2.1656E+06
273	2.6399E+06	2.4816E+06	3.9261E+06	4.2468E+06
280	3.7993E+06	3.5774E+06	5.5226E+06	5.9576E+06
290	6.2020E+06	5.8532E+06	8.7535E+06	9.4093E+06
296	8.1928E+06	7.7420E+06	1.1379E+07	1.2207E+07
298	8.9674E+06	8.4775E+06	1.2391E+07	1.3285E+07
300	9.8036E+06	9.2718E+06	1.3479E+07	1.4442E+07
353	7.2446E+07	6.9137E+07	9.0104E+07	9.5231E+07

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