

# Supporting Information

## Mechanistic Insights into Oxidative Decomposition of *exo*-Tetrahydrodicyclopentadiene

Sun Hee Park,<sup>†,‡,#</sup> Cheong Hoon Kwon,<sup>†,#</sup> Joongyeon Kim,<sup>†</sup> Jeong Sik Han,<sup>§</sup> Byung Hun Jeong,<sup>§</sup>

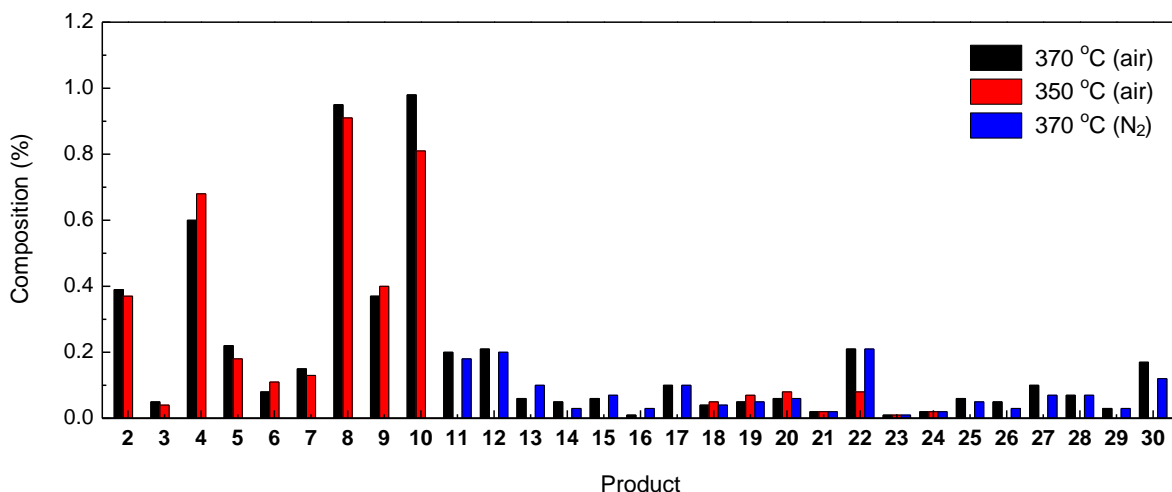
Hogyu Han,<sup>\*,||</sup> and Sung Hyun Kim<sup>\*,†</sup>

<sup>†</sup>Department of Chemical & Biological Engineering, Korea University, Seoul 136-701, Korea

<sup>‡</sup>Korea Atomic Energy Research Institute, 150 Deokjin-dong, Yuseong-gu, Daejeon 305-353, Korea






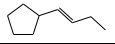





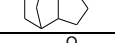
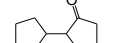
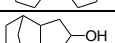
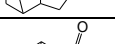
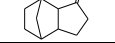
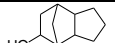
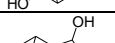
<sup>§</sup>Agency for Defense Development, 111 Sunam-dong, Yuseong-gu, Daejeon 305-152, Korea

<sup>||</sup>Department of Chemistry, Korea University, Seoul 136-701, Korea




























**Figure S1.** Comparison of product compositions obtained upon decomposition of *exo*-THDCP at 350 and 370 °C and 40 bar of air or N<sub>2</sub> for 7.5 h. See also Figure 2d–f. See Table 1 for the names, structures, and formulas of products **2–17**. Products **18–24** are the H<sub>2</sub> molecule and gaseous C<sub>1–4</sub> compounds as follows: **18**, hydrogen; **19**, methane; **20**, ethane; **21**, ethene; **22**, propane; **23**, propene; **24**, *n*-butane. Products **25–30** were detected at 370 °C, but could not be identified by GC–MS analysis. They are classified based on the retention time ( $t_R$ , min) in Tables S2 and S3 of the Supporting Information: **25**,  $t_R = 9.53$ ; **26**,  $t_R = 11.09$ ; **27**,  $t_R = 16.06$ ; **28**,  $t_R = 16.29$ ; **29**,  $t_R = 16.41$ ; **30**,  $t_R = 21.94$ .

**Table S1. Compositions of Products Formed upon Decomposition of *exo*-THDCP at 350 °C and 40 bar of air**

$t_R^a$ (min)	name	structure	formula	qual <sup>b</sup>	reaction time (h)								
					0.0	0.4	0.6	1.1	1.6	3.1	4.6	6.2	7.5
					composition (wt %)								
-	hydrogen		H <sub>2</sub>	-		0.01	0.01	0.02	0.03	0.03	0.04	0.04	0.05
-	methane		CH <sub>4</sub>	-		0.01	0.02	0.03	0.04	0.04	0.05	0.06	0.07
-	ethane		C <sub>2</sub> H <sub>6</sub>	-		0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08
-	ethene		C <sub>2</sub> H <sub>4</sub>	-		0.00	0.01	0.01	0.01	0.01	0.02	0.02	0.02
-	propane		C <sub>3</sub> H <sub>8</sub>	-		0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08
-	propene		C <sub>3</sub> H <sub>6</sub>	-					0.01	0.01	0.01	0.01	0.01
-	<i>n</i> -butane		C <sub>4</sub> H <sub>10</sub>	-			0.01	0.01	0.01	0.01	0.02	0.02	0.02
6.43	<i>trans</i> -1-butenylcyclopentane		C <sub>9</sub> H <sub>16</sub>	68		0.40	0.69	0.83	0.85	0.83	0.82	0.86	0.81
8.58	THDCP-1-ene		C <sub>10</sub> H <sub>14</sub>	95		0.05	0.09	0.25	0.38	0.58	0.72	0.82	0.91
8.72	<i>trans</i> -decalin		C <sub>10</sub> H <sub>18</sub>	97	0.52	0.51	0.52	0.52	0.52	0.52	0.52	0.51	0.52
8.90	<i>exo</i> -THDCP		C <sub>10</sub> H <sub>16</sub>	98	98.3	96.2	94.9	94.5	94.4	94.4	94.4	94.3	94.2
9.20	adamantane		C <sub>10</sub> H <sub>16</sub>	98	0.64	0.63	0.64	0.63	0.64	0.64	0.65	0.65	0.66
9.34	<i>endo</i> -THDCP		C <sub>10</sub> H <sub>16</sub>	99	0.55	0.53	0.55	0.56	0.55	0.56	0.58	0.60	0.62
11.35	2-cyclopentylcyclopentanone		C <sub>10</sub> H <sub>16</sub> O	81		0.25	0.35	0.38	0.38	0.39	0.39	0.38	0.40
12.18	THDCP-2-ol		C <sub>10</sub> H <sub>16</sub> O	-		0.79	1.18	1.17	1.08	0.94	0.82	0.73	0.68
12.25	THDCP-1-one		C <sub>10</sub> H <sub>14</sub> O	99		0.10	0.14	0.14	0.12	0.10	0.08	0.04	0.04
12.29	THDCP-5-ol		C <sub>10</sub> H <sub>16</sub> O	99		0.15	0.22	0.22	0.20	0.17	0.14	0.12	0.11
12.36	THDCP-1-ol		C <sub>10</sub> H <sub>16</sub> O	97		0.26	0.42	0.44	0.42	0.39	0.38	0.36	0.37
12.47	THDCP-5-one		C <sub>10</sub> H <sub>14</sub> O	99		0.05	0.09	0.10	0.11	0.10	0.12	0.12	0.13
12.69	THDCP-2-one		C <sub>10</sub> H <sub>14</sub> O	95		0.07	0.11	0.12	0.13	0.14	0.17	0.17	0.18

















<sup>a</sup>GC-MS retention time. <sup>b</sup>Wiley Library Quality.

**Table S2. Compositions of Products Formed upon Decomposition of *exo*-THDCP at 370 °C and 40 bar of air**

$t_R^a$ (min)	name	structure	formula	qual <sup>b</sup>	reaction time (h)									
					0.0	0.4	0.7	1.2	1.7	3.2	4.7	6.2	7.5	
					composition (wt %)									
-	hydrogen		H <sub>2</sub>	-										
-	methane		CH <sub>4</sub>	-		0.01	0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05
-	ethane		C <sub>2</sub> H <sub>6</sub>	-		0.01	0.02	0.02	0.03	0.04	0.05	0.05	0.06	
-	ethene		C <sub>2</sub> H <sub>4</sub>	-			0.01	0.01	0.01	0.01	0.02	0.02	0.02	
-	propane		C <sub>3</sub> H <sub>8</sub>	-		0.03	0.05	0.08	0.11	0.13	0.16	0.18	0.21	
-	propene		C <sub>3</sub> H <sub>6</sub>	-					0.01	0.01	0.01	0.01	0.01	
-	<i>n</i> -butane		C <sub>4</sub> H <sub>10</sub>	-			0.01	0.01	0.01	0.01	0.02	0.02	0.02	
2.14	cyclopentene		C <sub>5</sub> H <sub>8</sub>	90				0.01	0.03	0.05	0.07	0.10	0.10	
2.18	cyclopentane		C <sub>5</sub> H <sub>10</sub>	59									0.01	
6.43	<i>trans</i> -1-butenylcyclopentane		C <sub>9</sub> H <sub>16</sub>	76		0.39	0.93	1.02	1.04	1.01	1.01	1.03	0.98	
8.58	THDCP-1-ene		C <sub>10</sub> H <sub>14</sub>	94		0.05	0.12	0.34	0.45	0.69	0.82	0.90	0.95	
8.71	<i>trans</i> -decalin		C <sub>10</sub> H <sub>18</sub>	95	0.52	0.52	0.52	0.52	0.54	0.55	0.56	0.58	0.60	
8.90	<i>exo</i> -THDCP		C <sub>10</sub> H <sub>16</sub>	99	98.3	96.1	94.2	93.7	93.3	93.1	92.7	92.4	92.1	
8.96	4-methyl-2,3,4,5,6,7-hexahydro-1H-indene		C <sub>10</sub> H <sub>16</sub>	89			0.01	0.02	0.02	0.05	0.11	0.16	0.20	
9.10	cyclopentylcyclopentane		C <sub>10</sub> H <sub>18</sub>	96			0.02	0.02	0.03	0.04	0.04	0.05	0.06	
9.20	adamantane		C <sub>10</sub> H <sub>16</sub>	97	0.64	0.64	0.68	0.70	0.74	0.78	0.81	0.85	0.88	
9.34	<i>endo</i> -THDCP		C <sub>10</sub> H <sub>16</sub>	99	0.55	0.56	0.58	0.59	0.62	0.75	0.85	0.95	1.05	
9.40	1-cyclopentylcyclopentene		C <sub>10</sub> H <sub>16</sub>	97			0.01	0.02	0.04	0.06	0.11	0.16	0.21	
9.53				50		0.01	0.05	0.05	0.05	0.05	0.06	0.06	0.06	
10.04	bicyclopentylidene		C <sub>10</sub> H <sub>16</sub>	96		0.01	0.02	0.02	0.03	0.03	0.04	0.04	0.05	
10.19	2,3-dihydro-1-methyl-1H-indene		C <sub>10</sub> H <sub>12</sub>	94			0.01	0.02	0.02	0.03	0.04	0.05	0.06	
11.09				76			0.01	0.01	0.02	0.03	0.03	0.04	0.05	
11.35	2-cyclopentylcyclopentanone		C <sub>10</sub> H <sub>16</sub> O	50		0.24	0.36	0.39	0.40	0.39	0.39	0.37	0.37	
12.18	THDCP-2-ol		C <sub>10</sub> H <sub>16</sub> O	-		0.78	1.33	1.30	1.21	0.98	0.83	0.68	0.60	
12.25	THDCP-1-one		C <sub>10</sub> H <sub>14</sub> O	99		0.10	0.16	0.14	0.12	0.08	0.07	0.06	0.05	
12.29	THDCP-5-ol		C <sub>10</sub> H <sub>16</sub> O	99		0.15	0.23	0.22	0.21	0.16	0.13	0.10	0.08	
12.36	THDCP-1-ol		C <sub>10</sub> H <sub>16</sub> O	95		0.26	0.45	0.47	0.46	0.44	0.41	0.39	0.39	
12.47	THDCP-5-one		C <sub>10</sub> H <sub>14</sub> O	99		0.05	0.09	0.10	0.12	0.12	0.13	0.14	0.15	
12.69	THDCP-2-one		C <sub>10</sub> H <sub>14</sub> O	97		0.07	0.10	0.13	0.16	0.20	0.20	0.22	0.22	
16.06				58				0.02	0.03	0.05	0.06	0.08	0.10	
16.29				50				0.01	0.02	0.03	0.04	0.05	0.06	
16.41				47				0.01	0.01	0.02	0.02	0.03	0.03	
21.94				47				0.01	0.03	0.05	0.07	0.09	0.12	

<sup>a</sup>GC-MS retention time. <sup>b</sup>Wiley Library Quality.

**Table S3. Compositions of Products Formed upon Decomposition of *exo*-THDCP at 370 °C and 40 bar of N<sub>2</sub>**

<i>t<sub>R</sub></i> <sup>a</sup> (min)	name	structure	formula	qual <sup>b</sup>	reaction time (h)								
					0.0	0.4	0.7	1.2	2.0	3.2	4.7	6.2	7.5
					composition (wt %)								
-	hydrogen		H <sub>2</sub>	-		0.01	0.01	0.02	0.02	0.03	0.03	0.04	0.04
-	methane		CH <sub>4</sub>	-		0.01	0.01	0.02	0.03	0.03	0.04	0.04	0.05
-	ethane		C <sub>2</sub> H <sub>6</sub>	-		0.01	0.02	0.02	0.03	0.04	0.05	0.05	0.06
-	ethene		C <sub>2</sub> H <sub>4</sub>	-			0.01	0.01	0.01	0.01	0.02	0.02	0.02
-	propane		C <sub>3</sub> H <sub>8</sub>	-		0.03	0.05	0.08	0.11	0.13	0.16	0.18	0.21
-	propene		C <sub>3</sub> H <sub>6</sub>	-					0.01	0.01	0.01	0.01	0.01
-	<i>n</i> -butane		C <sub>4</sub> H <sub>10</sub>	-			0.01	0.01	0.01	0.01	0.02	0.02	0.02
2.14	cyclopentene		C <sub>5</sub> H <sub>8</sub>	90			0.01	0.02	0.04	0.06	0.08	0.09	0.10
2.18	cyclopentane		C <sub>5</sub> H <sub>10</sub>	78						0.01	0.01	0.01	0.03
8.75	<i>trans</i> -decalin		C <sub>10</sub> H <sub>18</sub>	86	0.52	0.53	0.54	0.55	0.56	0.56	0.57	0.58	0.58
8.95	<i>exo</i> -THDCP		C <sub>10</sub> H <sub>16</sub>	97	98.3	98.1	97.9	97.6	97.3	97.1	96.7	96.4	96.1
9.00	4-methyl-2,3,4,5,6,7-hexahydro-1H-indene		C <sub>10</sub> H <sub>16</sub>	94		0.01	0.03	0.05	0.08	0.11	0.14	0.16	0.18
9.06	cyclopentylcyclopentane		C <sub>10</sub> H <sub>18</sub>	94			0.02	0.03	0.04	0.06	0.07	0.09	0.10
9.23	adamantane		C <sub>10</sub> H <sub>16</sub>	96	0.64	0.68	0.70	0.73	0.76	0.79	0.81	0.84	0.85
9.38	<i>endo</i> -THDCP		C <sub>10</sub> H <sub>16</sub>	97	0.55	0.59	0.62	0.65	0.70	0.75	0.81	0.90	0.99
9.44	1-cyclopentylcyclopentene		C <sub>10</sub> H <sub>16</sub>	97		0.02	0.04	0.06	0.09	0.12	0.15	0.18	0.20
9.53				50		0.01	0.01	0.02	0.02	0.03	0.03	0.04	0.05
10.04	bicyclopentylidene		C <sub>10</sub> H <sub>16</sub>	96		0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.03
10.19	2,3-dihydro-1-methyl-1H-indene		C <sub>10</sub> H <sub>12</sub>	94			0.01	0.03	0.04	0.04	0.05	0.06	0.07
11.09				76			0.01	0.01	0.01	0.02	0.02	0.03	0.03
16.06				38				0.01	0.02	0.03	0.05	0.06	0.07
16.29				58				0.01	0.01	0.03	0.05	0.06	0.07
16.41				47					0.01	0.01	0.01	0.02	0.03
21.94				68			0.01	0.03	0.05	0.06	0.08	0.10	0.12

<sup>a</sup>GC-MS retention time. <sup>b</sup>Wiley Library Quality.