Supporting Information

The role of branching on the rate and mechanism of C–C cleavage in alkanes on metal surface

David D. Hibbitts[1,2], David W. Flaherty[1,3], Enrique Iglesia[1*]

[1] Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States

[2]Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, United States

[3]Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, United States

*Corresponding Author: iglesia@berkeley.edu

Table of Contents

List of Figures and Tables

Details of Density Functional Calculations of Thermochemical Properties

The enthalpy of a given state can be written as the sum of the DFT-derived energy (E_0), zero-point vibrational enthalpy (*ZPVE*) and vibrational, translational and rotational enthalpy (H_{vib}, H_{trans} and H_{rot}):

$$H = E_0 + ZPVE + H_{vib} + H_{trans} + H_{rot} \quad \text{(S1)}$$

similarly, the free energy of a state can be written as:

$$G = E_0 + ZPVE + G_{vib} + G_{trans} + G_{rot} \quad \text{(S2)}$$

and entropy can be determined for a state with a known H and G at a given T:

$$S = \frac{H - G}{T} \quad \text{(S3)}$$

For calculations which include a periodic Ir(111) surface (including adsorbed species and transition states on that surface), there are no translational or rotational degrees of freedom and DFT-derived vibrational frequencies can be used to determine the *ZPVE*, H_{vib} and G_{vib} shown in Eqns. S4-6).

$$ZPVE = \sum_i (½ \nu_i h) \quad \text{(S4)}$$

$$H_{vib} = \sum_i \left(\frac{\nu_i h e^{\frac{-\nu_i h}{kT}}}{1 - e^{\frac{-\nu_i h}{kT}}} \right) \quad \text{(S5)}$$

$$G_{vib} = \sum_i \left(-kT \ln \frac{1}{1 - e^{\frac{-\nu_i h}{kT}}} \right) \quad \text{(S6)}$$

Gas)phase molecules have translational and rotational degrees of freedom; thus H_{trans}, H_{rot}, G_{trans} and G_{rot} must also be computed:

$$H_{trans} = {}^5/_2\, kT \quad \text{(S7)}$$

$$H_{rot,linear} = kT \quad \text{(S8)}$$

$$H_{rot,nonlinear} = {}^3/_2\, kT \quad \text{(S9)}$$

$$G_{trans} = -kT \ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2} V\right] \quad \text{(S10)}$$

$$G_{rot} = -kT \ln\left[\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\theta_x\theta_y\theta_z}\right)^{1/2}\right] \quad \text{(S11)}$$

$$\theta_i = \frac{h^2}{8\pi^2 I_i k} \quad \text{(S12)}$$

where I_i is the moment of inertia about axes x, y or z and σ is the symmetry number of the molecule, 2 for H_2, 12 for CH_4 and 6 for C_2H_6, etc. Equations S10-S12 obtained from: McQuarrie, D. A.; *Statistical Mechanics*; Sausolito, CA.

Table S1. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values for C–C activations of ethane, propane, butane, and isobutane in α,β-bound intermediates via *$CH_{0–3}$–$CH_{0–1}$(R)R'*$^{\neq}$ transition states.

								ΔH_{act}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
	y	ℓ	λ	R	R'		**C**	kJ mol^{-1}		J mol^{-1} K^{-1}	kJ mol^{-1}
CH_3–C(R)R'	1	2	1.5	H	H	*CH_3–CH_2*	2	136	251	–67	291
				CH_3	H	*CH_3–$CHCH_3$*	3	163	280	–45	306
				CH_3CH_2	H	*CH_3–$CHCH_2CH_3$*	4	164	288	–48	316
				CH_3	CH_3	*CH_3–C*(CH_3)CH_3	4	161	297	–81	345
CH_2–CH(R)R'	1	2	1.5	H	H	*CH_3–CH_2*	2	136	251	–67	291
				CH_3	H	*CH_3CH_2–CH_2*	3	147	261	–52	292
				CH_3CH_2	H	*$CH_3CH_2CH_2$–CH_2*	4	150	257	–79	303
				CH_3	CH_3	*CH_2–CH*(CH_3)CH_3	4	149	265	–54	297
CH_2–C(R)R'	2	2	2.0	H	H	*CH_2–CH_2*	2	148	277	6	274
				CH_3	H	*CH_3CH–CH_2*	3	129	264	–3	266
				CH_3CH_2	H	*CH_3CH_2CH–CH_2*	4	117	254	–32	273
				CH_3	CH_3	*CH_2–C*(CH_3)CH_3	4	102	255	10	249
CH–CH(R)R'	2	2	2.0	H	H	*CH_3–CH*	2	95	231	5	229
				CH_3	H	*CH_3CH_2–CH*	3	100	235	–3	236
				CH_3CH_2	H	*$CH_3CH_2CH_2$–CH*	4	98	235	0	235
				CH_3	CH_3	*CH–CH*(CH_3)CH_3	4	98	235	–1	236
CH–C(R)R'	3	2	2.5	H	H	*CH_2–CH*	2	108	259	64	221
				CH_3	H	*CH_3CH–CH*	3	82	233	54	201
				CH_3CH_2	H	*CH_3CH_2CH–CH*	4	82	236	55	204
				CH_3	CH_3	*CH–C*(CH_3)CH_3	4	59	224	57	190
C–CH(R)R'	3	2	2.5	H	H	*CH_3–C*	2	202	281	73	238
				CH_3	H	*CH_3CH_2–C*	3	202	283	64	246
				CH_3CH_2	H	*$CH_3CH_2CH_2$–C*	4	203	284	61	248
				CH_3	CH_3	*C–CH*(CH_3)CH_3	4	216	305	47	277
C–C(R)R'	4	2	3.0	H	H	*CH_2–C*	2	211	358	133	279
				CH_3	H	*CH_3CH–C*	3	185	321	125	247
				CH_3CH_2	H	*CH_3CH_2CH–C*	4	185	321	125	247
				CH_3	CH_3	*C–C*(CH_3)CH_3	4	168	307	133	228

Table S2. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values for C–C activations of propane, isobutane, and neopentane in α,γ-bound intermediates via *$CH_{0-2}C^*(R)(R')–CH_{0-2}$*$^{\neq}$ transition states.

								ΔH_{act}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
	y	*ℓ*	*λ*	R	R'		**C**	kJ mol^{-1}		J mol^{-1} K^{-1}	kJ mol^{-1}
$CH_2C(R)(R')–CH_2$	2	2[a]	2.0	H	H	*$CH_2CH_2–CH_2$*	3	171	319	1	318
				CH_3	H	*$CH_2CH(CH_3)–CH_2$*	4	141	309	–10	315
				CH_3	CH_3	*$CH_2C(CH_3)_2–CH_2$*	5	133	306	3	305
$CHC(R)(R')–CH_2$	3	3	3.0	H	H	*$CHCH_2$*$–CH_2$*	3	134	327	64	290
				CH_3	H	*$CHCH^*(CH_3)–CH_2$*	4	134	334	70	293
				CH_3	CH_3	*$CHC^*(CH_3)_2–CH_2$*	5	143	346	84	296
$CH_2C(R)(R')–CH$	3	2[a]	2.5	H	H	*$CH_2CH_2–CH$*	3	106	282	62	246
				CH_3	H	*$CH_2CH(CH_3)–CH$*	4	91	274	59	239
				CH_3	CH_3	*$CH_2C(CH_3)_2–CH$*	5	78	264	44	238
$CC(R)(R')–CH_2$	4	3	3.5	H	H	*CCH_2*$–CH_2$*	3	128	312	128	237
				CH_3	H	*$CCH^*(CH_3)–CH_2$*	4	93	303	132	225
				CH_3	CH_3	*$CC^*(CH_3)_2–CH_2$*	5	86	303	161	208
$CH_2C(R)(R')–C$	4	2[a]	3.0	H	H	*$CH_2CH_2–C$*	3	170	337	128	261
				CH_3	H	*$CH_2CH(CH_3)–C$*	4	160	322	124	249
				CH_3	CH_3	*$CH_2C(CH_3)_2–C$*	5	149	313	138	231
$CHC(R)(R')–CH$	4	3	3.5	H	H	*$CHCH_2$*$–CH$*	3	67	309	120	238
				CH_3	H	*$CHCH^*(CH_3)–CH$*	4	67	311	124	238
				CH_3	CH_3	*$CHC^*(CH_3)_2–CH$*	5	75	325	140	242
$CC(R)(R')–CH$	5	3	4.0	H	H	*CCH_2*$–CH$*	3	62	318	187	207
				CH_3	H	*$CCH^*(CH_3)–CH$*	4	58	310	192	196
				CH_3	CH_3	*$CC^*(CH_3)_2–CH$*	5	54	308	213	182
$CHC(R)(R')–C$	5	3	4.0	H	H	*$CHCH_2$*$–C$*	3	136	391	189	279
				CH_3	H	*$CHCH^*(CH_3)–C$*	4	141	375	173	273
				CH_3	CH_3	*$CHC^*(CH_3)_2–C$*	5	136	390	210	266
$CC(R)(R')–C$	6	3	4.5	H	H	*CCH_2*$–C$*	3	46	372	251	223
				CH_3	H	*$CCH^*(CH_3)–C$*	4	38	360	257	207
				CH_3	CH_3	*$CC^*(CH_3)_2–C$*	5	35	356	274	194

[a] Concerted alkene (g) formation reduces the site requirements as the 'central' C-atom does not ever bind to the catalyst surface.

Table S3. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values for C–C activations of isobutane and neopentane in α,γ,δ-bound intermediates via *$CH_{0–2}CH(CH_{0–2}*)$–$CH_{0–2}$*$^{\neq}$ transition states.

							ΔH_{act}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
	y	ℓ	λ	R		**C**	kJ mol^{-1}		J mol^{-1} K^{-1}	kJ mol^{-1}
$CH_2CR(CH_2*)$–CH_2	3	4	3.5	H	*$CH_2CH(CH_2*)$–CH_2*	4	155	360	56	327
				CH_3	*$CH_2C(CH_3)(CH_2*)$–CH_2*	5	157	368	83	319
$CH_2CR(CH*)$–CH_2	4	4	4.0	H	*$CH_2CH(CH*)$–CH_2*	4	80	373	155	281
				CH_3	*$CH_2C(CH_3)(CH*)$–CH_2*	5	69	362	178	257
$CH_2CR(CH_2*)$–CH	4	4	4.0	H	*$CH_2CH(CH_2*)$–CH*	4	182	462	134	383
				CH_3	*$CH_2C(CH_3)(CH_2*)$–CH*	5	172	462	173	359
$CH_2CR(C*)$–CH_2	5	4	4.5	H	*$CH_2CH(C*)$–CH_2*	4	158	478	221	347
				CH_3	*$CH_2C(CH_3)(C*)$–CH_2*	5	144	451	241	308
$CH_2CR(CH_2*)$–C	5	4	4.5	H	*$CH_2CH(CH_2*)$–C*	4	217	527	204	406
				CH_3	*$CH_2C(CH_3)(CH_2*)$–C*	5	211	494	200	375
$CHCR(CH*)$–CH_2	5	4	4.5	H	*$CHCH(CH*)$–CH_2*	4	120	439	194	325
				CH_3	*$CHC(CH_3)(CH*)$–CH_2*	5	126	439	214	312
$CH_2CR(CH*)$–CH	5	4	4.5	H	*$CH_2CH(CH*)$–CH*	4	56	376	193	261
				CH_3	*$CH_2C(CH_3)(CH*)$–CH*	5	54	365	211	240
$CHCR(C*)$–CH_2	6	4	5.0	H	*$CHCH(C*)$–CH_2*	4	113	474	267	316
				CH_3	*$CHC(C)(CH_2*)$–CH_2*	5	107	455	289	284
$CH_2CR(C*)$–CH	6	4	5.0	H	*$CH_2CH(C*)$–CH*	4	70	431	266	273
				CH_3	*$CH_2C(CH_3)(C*)$–CH*	5	62	407	285	238
$CH_2CR(CH*)$–C	6	4	5.0	H	*$CH_2CH(CH*)$–C*	4	86	443	260	289
				CH_3	*$CH_2C(CH_3)(CH*)$–C*	5	89	430	278	266
$CCR(C*)$–CH_2	7	4	5.5	H	*$CCH(C*)$–CH_2*	4	115	565	334	367
				CH_3	*$CC(CH_3)(C*)$–CH_2*	5	111	542	359	329
$CH_2CR(C*)$–C	7	4	5.5	H	*$CH_2CH(C*)$–C*	4	57	505	331	309
				CH_3	*$CH_2C(CH_3)(C*)$–C*	5	54	479	351	271
$CHCR(CH*)$–CH	6	4	5.0	H	*$CHCH(CH*)$–CH*	4	38	452	262	297
				CH_3	*$CHC(CH_3)(CH*)$–CH*	5	32	423	281	256
$CHCR(C*)$–CH	7	4	5.5	H	*$CHCH(C*)$–CH*	4	33	472	325	279
				CH_3	*$CHC(CH_3)(C*)$–CH*	5	29	446	345	242
$CHCR(CH*)$–C	7	4	5.5	H	*$CHCH(CH*)$–C*	4	101	538	321	348
				CH_3	*$CHC(CH_3)(CH*)$–C*	5	104	520	342	317
$CCR(C*)$–CH	8	4	6.0	H	*$CCH(C*)$–CH*	4	54	563	394	329
				CH_3	*$CC(CH_3)(C*)$–CH*	5	48	533	415	287
$CHCR(C*)$–C	8	4	6.0	H	*$CHCH(C*)$–C*	4	41	549	392	316
				CH_3	*$CHC(CH_3)(C*)$–C*	5	36	520	413	275
$CCR(C*)$–C	9	4	6.5	H	*$CCH(C*)$–C*	4	36	639	459	367
				CH_3	*$CC(CH_3)(C*)$–C*	5	29	604	478	321

Table S4. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values for C–C activations of propane and isobutane in α,β,γ-bound intermediates via *$CH_{0-2}C^*(R)–CH_{0-2}^*$ $^{\neq}$ transition states.

							ΔH_{act}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
	y	ℓ	λ	R		**C**	kJ mol^{-1}		J mol^{-1} K^{-1}	kJ mol^{-1}
*$CH_2C^*(R)–CH_2^*$	3	3	3.0	H	*$CH_2CH^*–CH_2^*$	3	138	301	63	264
				CH_3	*$CH_2C^*(CH_3)–CH_2^*$	4	114	288	64	250
*$CHC^*(R)–CH_2^*$	4	3	3.5	H	*$CHCH^*–CH_2^*$	3	94	302	119	231
				CH_3	*$CHC^*(CH_3)–CH_2^*$	4	82	287	108	223
*$CH_2C^*(R)–CH^*$	4	3	3.5	H	*$CH_2CH^*–CH^*$	3	111	319	121	248
				CH_3	*$CH_2C^*(CH_3)–CH^*$	4	64	269	123	196
*$CC^*(R)–CH_2^*$	5	3	4.0	H	*$CCH^*–CH_2^*$	3	164	375	218	246
				CH_3	*$CC^*(CH_3)–CH_2^*$	4	154	354	207	232
*$CH_2C^*(R)–C^*$	5	3	4.0	H	*$CH_2CH^*–C^*$	3	199	410	189	298
				CH_3	*$CH_2C^*(CH_3)–C^*$	4	204	405	253	255
*$CHC^*(R)–CH^*$	5	3	4.0	H	*$CHCH^*–CH^*$	3	82	339	189	227
				CH_3	*$CHC^*(CH_3)–CH^*$	4	81	325	193	210
*$CC^*(R)–CH^*$	6	3	4.5	H	*$CCH^*–CH^*$	3	117	377	255	226
				CH_3	*$CC^*(CH_3)–CH^*$	4	112	351	269	190
*$CHC^*(R)–C^*$	6	3	4.5	H	*$CHCH^*–C^*$	3	167	427	251	279
				CH_3	*$CHC^*(CH_3)–C^*$	4	186	425	262	269
*$CC^*(R)–C^*$	7	3	5.0	H	*$CCH^*–C^*$	3	123	485	328	291
				CH_3	*$CC^*(CH_3)–C^*$	4	121	454	331	258

Table S5. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values for C–C activations of propane and isobutane in $\alpha,\beta,\gamma,\delta$-bound intermediates via $*CH_{0-2}C*(CH_{0-2}*)–CH_{0-2}*^{\neq}$ transition states.

y	ℓ	λ		ΔH_{act} kJ mol^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$ J mol^{-1} K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}
4	4	4.0	*CH$_2$C*(CH$_2$*)–CH$_2$*	179	352	140	269
5	4	4.5	*CH$_2$C*(CH*)–CH$_2$*	130	388	198	271
5	4	4.5	*CH$_2$C*(CH$_2$*)–CH*	113	371	198	254
6	4	5.0	*CH$_2$C*(C*)–CH$_2$*	238	539	277	375
6	4	5.0	*CH$_2$C*(CH$_2$*)–C*	183	485	278	320
6	4	5.0	*CHC*(CH*)–CH$_2$*	142	444	263	288
6	4	5.0	*CH$_2$C*(CH*)–CH*	98	402	266	244
7	4	5.5	*CHC*(C*)–CH$_2$*	172	539	336	340
7	4	5.5	*CH$_2$C*(C*)–CH*	118	486	336	287
7	4	5.5	*CH$_2$C*(CH*)–C*	126	493	334	295
8	4	6.0	*CC*(C*)–CH$_2$*	167	634	402	396
8	4	6.0	*CH$_2$C*(C*)–C*	115	582	402	344
7	4	5.5	*CHC*(CH*)–CH*	39	531	334	333
8	4	6.0	*CHC*(C*)–CH*	61	574	398	338
8	4	6.0	*CHC*(CH*)–C*	68	580	397	345
9	4	6.5	*CC*(C*)–CH*	72	626	462	353
9	4	6.5	*CH$_2$C*(C*)–C*	73	628	461	354
10	4	7.0	*CC*(C*)–C*	47	747	531	432

Table S6. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values for C–C activations of ethane, propane, butane, isobutane, and neopentane in α-bound intermediates via $*CH_{0-2}–C(R)(R')R''*^{\neq}$ transition states.

									ΔH_{act}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
	y	ℓ	λ	R	R'	R''		**C**	kJ mol^{-1}		J mol^{-1} K^{-1}	kJ mol^{-1}
$*CH_2–C*(R)(R')R''$	1	2	1.5	H	H	H	$*CH_3–CH_2*$	2	136	251	–67	291
				CH_3	H	H	$*CH_3CH_2–CH_2*$	3	147	261	–52	292
				CH_3CH_2	H	H	$*CH_3CH_2CH_2–CH_2*$	4	150	257	–79	303
				CH_3	CH_3	H	$*CH_2–CH*(CH_3)_2$	4	149	265	–54	297
				CH_3	CH_3	CH_3	$*CH_2–C*(CH_3)_3$	5	138	266	–51	296
$*CH–C*(R)(R')R''$	2	2	2.0	H	H	H	$*CH_3–CH*$	2	95	231	5	229
				CH_3	H	H	$*CH_3CH_2–CH*$	3	100	235	–3	236
				CH_3CH_2	H	H	$*CH_3CH_2CH_2–CH*$	4	98	235	0	235
				CH_3	CH_3	H	$*CH–CH*(CH_3)_2$	4	96	235	–1	236
				CH_3	CH_3	CH_3	$*CH–C*(CH_3)_3$	5	92	258	9	253
$*C–C*(R)(R')R''$	3	2	2.5	H	H	H	$*CH_3–C*$	2	202	281	73	238
				CH_3	H	H	$*CH_3CH_2–C*$	3	202	283	64	246
				CH_3CH_2	H	H	$*CH_3CH_2CH_2–C*$	4	203	284	61	248
				CH_3	CH_3	H	$*C–CH*(CH_3)_2$	4	216	305	47	277
				CH_3	CH_3	CH_3	$*C–C*(CH_3)_3$	5	217	309	51	279

Table S7. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values for ^3C–^3C activations of 2,3-dimethylbutane.

							ΔH_{act}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
y	ℓ	λ					kJ mol^{-1}		J mol^{-1} K^{-1}	kJ mol^{-1}
1	2	1.5	$CH_3CH(CH_3)C^*(CH_3)CH_3$	to	$CH_3CH^*CH_3$	$CH_3C^*CH_3$	165	325	–55	358
2	2	2	$CH_3CH(CH_3)C^*(CH_3)CH_2^*$	to	$CH_3CH^*CH_3$	$CH_3C^*CH_2^*$	152	316	–29	333
2	2	2	$CH_3C^*(CH_3)CH(CH_3)CH_2^*$	to	$CH_3C^*CH_3$	$CH_3CH^*CH_2^*$	115	312	–9	318
2	2	2	$CH_3C^*(CH_3)C^*(CH_3)CH_3$	to	$CH_3C^*CH_3$	$CH_3C^*CH_3$	92	284	–1	285
2	2	2	$CH2^*CH(CH_3)CH(CH_3)CH_2^*$	to	$CH_3CH^*CH_2^*$	$CH_3CH^*CH_2^*$	128	351	–17	361
3	3	3	$CH_3CH(CH_3)C^*(CH_3)CH^*$	to	$CH_3CH^*CH_3$	CH_3C^*CH	121	314	102	253
3	3	3	$CH_3C^*(CH_3)CH(CH_3)CH^*$	to	$CH_3C^*CH_3$	CH_3CH^*CH	130	362	53	330
3	3	3	$CH_3C^*(CH_3)C^*(CH_3)CH_2^*$	to	$CH_3C^*CH_3$	$CH_3C^*CH_2^*$	119	313	47	285
3	2	2.5	$CH2^*CH(CH_3)CH(CH_3)CH^*$	to	$CH_3CH^*CH_2^*$	CH_3CH^*CH	101	317	20	305
3	3	3	$CH2^*CH(CH_3)C^*(CH_3)CH_2^*$	to	$CH_3CH^*CH_2^*$	$CH_3C^*CH_2^*$	104	347	65	309
4	3	3.5	$CH_3CH(CH_3)C^*(CH_3)C^*$	to	$CH_3CH^*CH_3$	$CH_3C^*C^*$	225	374	131	296
4	3	3.5	$CH_3C^*(CH_3)CH(CH_3)C^*$	to	$CH_3C^*CH_3$	$CH_3CH^*C^*$	78	307	151	217
4	3	3.5	$CH_3C^*(CH_3)C^*(CH_3)CH^{**}$	to	$CH_3C^*CH_3$	CH_3C^*CH	81	307	115	239
4	2	3	$CH_2^*CH(CH_3)CH(CH_3)C^*$	to	$CH_3CH^*CH_2^*$	$CH_3CH^*C^*$	101	314	117	244
4	3	3.5	$CH_2^*CH(CH_3)C^*(CH_3)CH^*$	to	$CH_3CH^*CH_2^*$	$CH_3C^*CH_3$	77	361	91	307
4	4	4	$CH_2^*C^*(CH_3)CH(CH_3)CH^*$	to	$CH_3C^*CH_2^*$	CH_3CH^*CH	123	373	123	301
4	4	4	$CH_2^*C^*(CH_3)C^*(CH_3)CH_2^*$	to	$CH_3C^*CH_2^*$	$CH_3C^*CH_2^*$	145	356	121	285
5	3	4	$CH_3C^*(CH_3)C^*(CH_3)C^*$	to	$CH_3C^*CH_3$	$CH_3C^*C^*$	115	331	191	218
5	3	4	$CH_2^*CH(CH_3)C^*(CH_3)C^*$	to	$CH_3CH^*CH_2^*$	$CH_3C^*C^*$	137	394	184	284
5	4	4.5	$CH_2^*C^*(CH_3)CH(CH_3)C^*$	to	$CH_3C^*CH_2^*$	$CH_3CH^*C^*$	65	339	203	218
5	4	4.5	$CH_2^*C^*(CH_3)C^*(CH_3)CH^*$	to	$CH_3C^*CH_2^*$	CH_3C^*CH	121	347	192	233
5	4	4.5	$CH^*CH(CH_3)CH(CH_3)C^*$	to	$CH_3CH^*CH^*$	$CH_3CH^*C^*$	85	338	216	211
5	4	4.5	$CH^*CH(CH_3)C^*(CH_3)CH^*$	to	$CH_3CH^*CH^*$	CH_3C^*CH	92	371	186	260
6	4	5	$CH_2^*C^*(CH_3)C^*(CH_3)C^*$	to	$CH_3C^*CH_2^*$	$CH_3C^*C^*$	172	409	262	253
6	4	5	$CH^*CH(CH_3)C^*(CH_3)C^*$	to	$CH_3CH^*CH^*$	$CH_3C^*C^*$	190	446	271	285
6	4	5	$CH^*C^*(CH_3)CH(CH_3)C^*$	to	$CH_3C^*CH^*$	$CH_3CH^*C^*$	75	332	267	174
6	4	5	$CH^*C^*(CH_3)C^*(CH_3)CH^*$	to	$CH_3C^*CH^*$	$CH_3C^*CH^*$	113	356	253	206
6	2	4	$C^*CH(CH_3)CH(CH_3)C$	to	$CH_3CH^*C^*$	$CH_3CH^*C^*$	83	253	243	109
7	4	5.5	$CH^*C^*(CH_3)C^*(CH_3)C^*$	to	$CH_3C^*CH^*$	$CH_3C^*C^*$	182	445	332	248
7	4	5.5	$C^*CH(CH_3)C^*(CH_3)C^*$	to	$CH_3CH^*C^*$	$CH_3C^*C^*$	112	362	323	171
8	4	6	$C^*C^*(CH_3)C^*(CH_3)C^*$	to	$CH_3C^*C^*$	$CH_3C^*C^*$	159	428	400	191
6	6	6	$CH_2^*C^*(CH_2^*)C^*(CH_2^*)CH_2^*$	to	$CH_2^*C^*CH_2^*$	$CH_2^*C^*CH_2^*$	100	413	281	246
5	5	5	$CH_2^*C^*(CH_3)C^*(CH_2^*)CH_2^*$	to	$CH_3C^*CH_2^*$	$CH_2^*C^*CH_2^*$	115	385	210	261
4	4	4	$CH_3C^*(CH_3)C^*(CH_2^*)CH_2^*$	to	$CH_3C^*CH_3$	$CH_2^*C^*CH_2^*$	152	349	131	272
10	6	8	$CH^*C^*(CH^*)C^*(CH^*)CH^*$	to	$CH^*C^*CH^*$	$CH^*C^*CH^*$	95	608	527	295
14	6	10	$C^*C^*(C^*)C^*(C^*)C^*$	to	$C^*C^*C^*$	$C^*C^*C^*$	129	1037	825	548
13	6	9.5	$CH^*C^*(C^*)C^*(C^*)C^*$	to	$CH^*C^*C^*$	$C^*C^*C^*$	120	913	746	470
12	6	9	$CH^*C^*(CH^*)C^*(C^*)C^*$	to	$CH^*C^*CH^*$	$C^*C^*C^*$	98	792	668	396
12	6	9	$CH^*C^*(C^*)C^*(CH^*)C^*$	to	$CH^*C^*C^*$	$CH^*C^*C^*$	131	791	673	392
11	6	8.5	$CH^*C^*(CH^*)C^*(CH^*)C^*$	to	$CH^*C^*CH^*$	$CH^*C^*C^*$	112	698	600	342
3	4	3.5	$CH_3CH(CH_3)C^*(CH_2^*)CH_2^*$	to	$CH_3CH^*CH_3$	$CH_2^*C^*CH_2^*$	133	330	79	283
4	4	4	$CH_3CH(CH_3)C^*(CH_2^*)CH^*$	to	$CH_3CH^*CH_3$	$CH_2^*C^*CH^*$	157	368	150	279
5	4	4.5	$CH_3CH(CH_3)C^*(CH_2^*)C^*$	to	$CH_3CH^*CH_3$	$CH_2^*C^*C^*$	211	431	197	314
5	4	4.5	$CH_3CH(CH_3)C^*(CH^*)CH^*$	to	$CH_3CH^*CH_3$	$CH^*C^*CH^*$	151	414	207	291
3	4	3.5	$CH_3C^*(CH_3)CH(CH_2^*)CH_2^*$	to	$CH_3C^*CH_3$	$CH_2^*CH^*CH_2^*$	120	354	62	317
4	4	4	$CH_3C^*(CH_3)C^*(CH_2^*)CH_2^*$	to	$CH_3C^*CH_3$	$CH_2^*C^*CH_2^*$	159	352	133	274
4	4	4	$CH_3C^*(CH_3)CH(CH_2^*)CH^*$	to	$CH_3C^*CH_3$	$CH_2^*CH^*CH^*$	54	356	123	283
5	4	4.5	$CH_3C^*(CH_3)C^*(CH_2^*)CH^*$	to	$CH_3C^*CH_3$	$CH_2^*C^*CH^*$	149	417	190	305

5	4	4.5	$CH_3C^*(CH_3)CH(CH_2^*)C^*$	to	$CH_3C^*CH_3$	$CH_2^*CH^*C^*$	135	444	215	317
6	4	5	$CH_3C^*(CH_3)C^*(CH_2^*)C^*$	to	$CH_3C^*CH_3$	$CH_2^*C^*C^*$	193	539	279	374
5	4	4.5	$CH_3C^*(CH_3)CH(CH^*)CH^*$	to	$CH_3C^*CH_3$	CH^*CHCH^*	103	439	186	329
6	4	5	$CH_3C^*(CH_3)C^*(CH^*)CH^*$	to	$CH_3C^*CH_3$	$CH^*C^*CH^*$	152	446	257	294
6	4	5	$CH_3C^*(CH_3)CH(CH^*)C^*$	to	$CH_3C^*CH_3$	$CH^*CH^*C^*$	127	489	256	337
7	4	5.5	$CH_3C^*(CH_3)C^*(CH^*)C^*$	to	$CH_3C^*CH_3$	$CH^*C^*C^*$	249	555	331	359
7	4	5.5	$CH_3C^*(CH_3)CH(C^*)C^*$	to	$CH_3C^*CH_3$	$C^*CH^*C^*$	135	578	326	384
8	4	6	$CH_3C^*(CH_3)C^*(C^*)C^*$	to	$CH_3C^*CH_3$	$C^*C^*C^*$	263	649	396	414
3	5	4	$CH_3CH(CH_2)CH(CH_2^*)CH_2^*$	to	$CH_3CH^*CH_2^*$	$CH_2^*CH^*CH_2^*$	153	438	141	355
5	5	5	$CH_2^*CH(CH_2)CH(CH_3)C^*$	to	$CH_3CH^*C^*$	$CH_2^*CH^*CH_2^*$	48	376	202	256
6	5	5.5	$C^*C^*(CH_3)CH(CH_2^*)CH_2^*$	to	$CH_3C^*C^*$	$CH_2^*CH^*CH_2^*$	144	433	280	267
6	5	5.5	$CH^*C^*(CH_3)C^*(CH_2^*)CH_2^*$	to	$CH_3C^*CH^*$	$CH_2^*C^*CH_2^*$	94	364	267	206
7	5	6	$C^*CH(CH_3)CH(CH_2^*)C^*$	to	$CH_3CH^*C^*$	$CH_2^*CH^*C^*$	114	413	351	205
7	5	6	$C^*CH(CH_3)C^*(CH_2^*)CH^*$	to	$CH_3CH^*C^*$	$CH_2^*C^*CH^*$	78	397	340	195
7	5	6	$CH^*C^*(CH_3)C^*(CH_2^*)CH^*$	to	$CH_3C^*CH^*$	$CH_2^*C^*CH^*$	104	420	328	225
8	5	6.5	$C^*CH(CH_3)C^*(CH_2^*)C^*$	to	$CH_3CH^*C^*$	$CH_2^*C^*C^*$	134	469	394	235
8	5	6.5	$C^*C^*(CH_3)C^*(CH_2^*)CH^*$	to	$CH_3C^*C^*$	$CH_2^*C^*CH^*$	153	505	404	266
4	6	5	$CH_2^*CH(CH_2^*)CH(CH_2^*)CH_2^*$	to	$CH_2^*CH^*CH_2^*$	$CH_2^*CH^*CH_2^*$	135	499	174	396

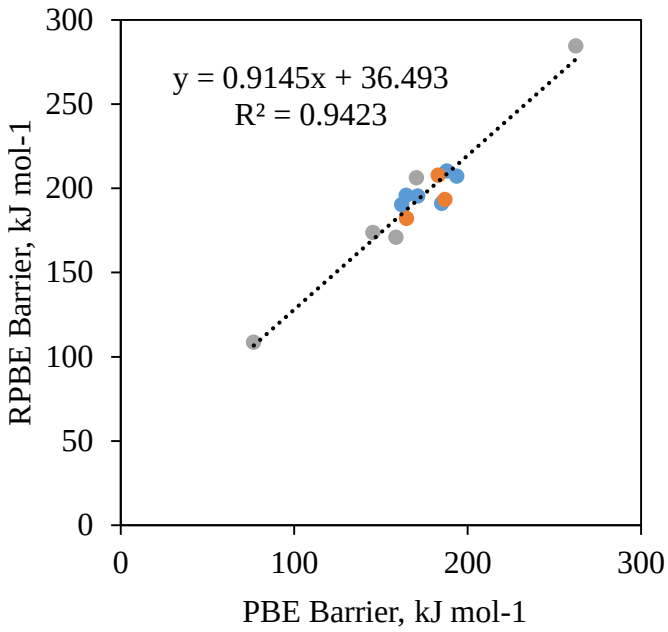

Figure S1. Comparisons of effective free energy barriers ($\Delta G^{\neq}$, kJ mol^{-1}) computed with the PBE and RPBE functionals. Six barriers for C–C cleavage of isobutane derived intermediates are shown in blue, three barriers for C–C cleavage of neopentane-derived intermediates are shown in orange, five barriers for C–C cleavage of 2,3-dimethylbutane-derived intermediates are shown in gray. An overall trend line (black) shows the strong linear relationship with a slope near unity.

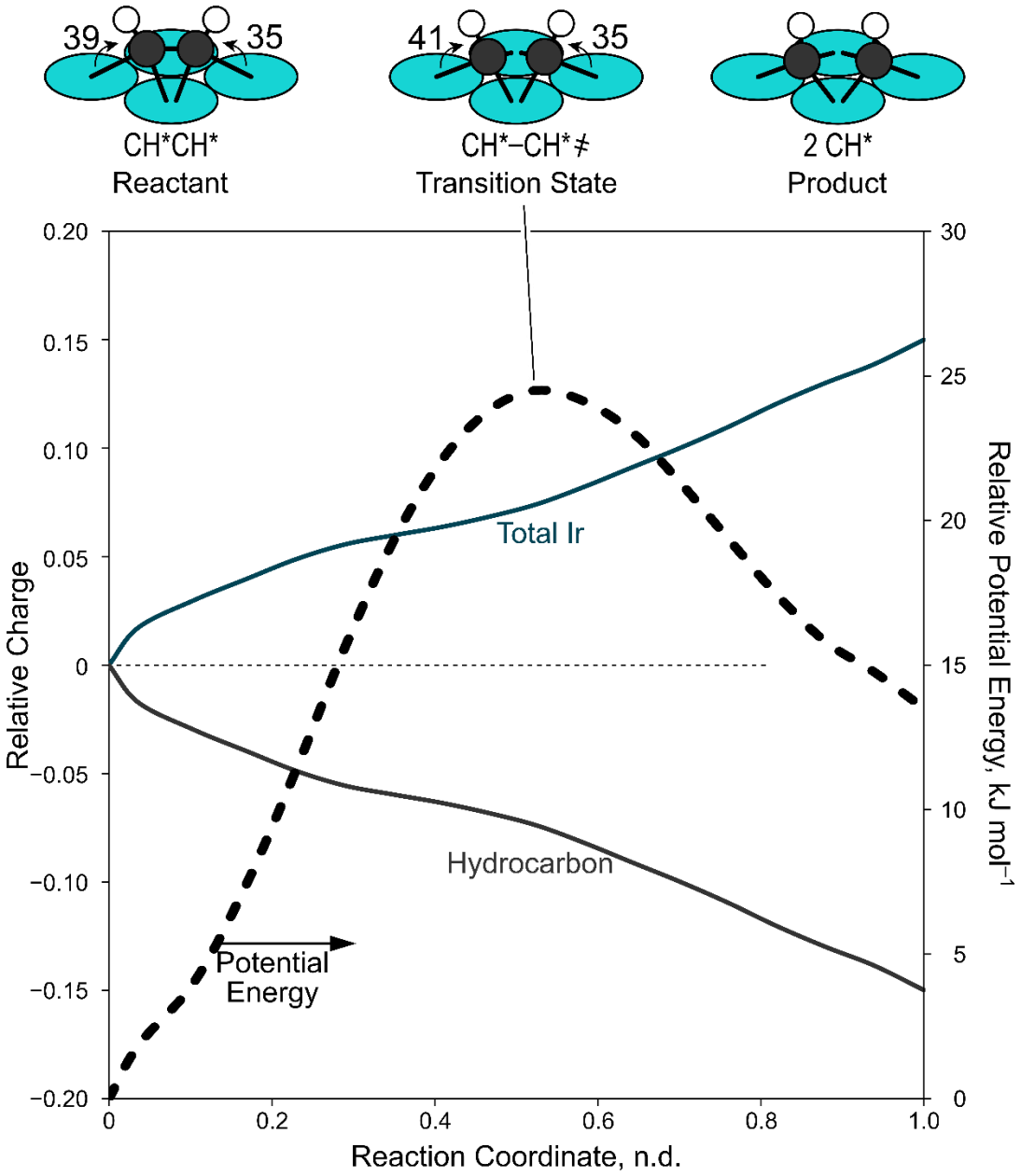

Figure S2. Reaction coordinate diagrams showing relative electronic energy (kJ mol^{-1} dashed lines) and charges (in e^-, solid lines) for C–C cleavage of ***A)*** ethane via CH*–CH*≠. Total partial charge on the Ir surface shown in blue and charges on the hydrocarbon are shown in gray in the online version. Above the plot are illustrations displaying reactant, transition state, and product structures as well as the charge transfer (in e^- x 10^3) to/from the surface and between hydrocarbon fragments for the C–C cleavage reaction.