Supporting Information

Effects of Chain Length on the Mechanism and Rates of Metal-Catalyzed Hydrogenolysis of n-Alkanes

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Details of Density Functional Calculations of Thermochemical Properties

VASP calculations were performed using PAW potentials with energy cutoffs of 400 eV. Exchange and correlations energies were computed using RPBE for Sections 3.1-3.3. Section 3.4 deals explicitly with the effects of van der Waals contributions and these contributions were accounted for using a variety of functionals: optB88-vdW, optB86-vdW, vdW-DF2, and BEEF.

Calculations of gas-phase species were performed in an 18 x 18 x 18 Å unit cell of vacuum and were computed using only a Γ-point sampling of the Brillouin zone. The Ir(111) surface was constructed with a 4x4 lattice using an experimentally-measured lattice parameter of 3.84 Å and four layers perpendicular to the (111) surface. The bottom two layers were fixed in their bulk positions while all other atoms were unconstrained.

All structures (including transition states) were converged until the force on all unconstrained atoms was < 0.05 eV/Å. Forces were computed using a 3 x 3 x 1 sampling of the Brillouin zone for structures involving the Ir(111) surface. After geometric convergence, a single-point calculation was performed using a 6 x 6 x 1 sampling to provide potential energies (E_0) of surface-bound reactant, transition, and product states.

Transition state structures were obtained using the dimer method, which was initialized by nudged elastic band (NEB) methods. NEB calculations were carried out using 16 images and the minimum energy pathway was optimized until the maximum normal force on all unconstrained atoms was < 0.30 eV/Å. NEB calculations only provide an estimate of the transition state structure and the reaction mode to initialize dimer calculations. Transition state structures and potential energies (E_0) presented in the paper were all obtained using the dimer method with forces on all unconstrained atoms < 0.05 eV/Å. Vibrational frequency calculations were then performed to verify a single imaginary mode (negative frequency) for all transition states described in this work.

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}):

$$H = E_0 + ZPVE + H_{vib} + H_{trans} + H_{rot} \tag{S1}$$

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

$$G = E_0 + ZPVE + G_{vib} + G_{trans} + G_{rot} \tag{S2}$$

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

$$S = \frac{H - G}{T} \tag{S3}$$

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).

$$ZPVE = \sum_i (\tfrac{1}{2}v_i h) \tag{S4}$$

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

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

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

$$H_{trans} = \tfrac{5}{2} kT \tag{S7}$$

$$H_{rot,linear} = kT \tag{S8}$$

$$H_{rot,nonlinear} = \tfrac{3}{2} kT \tag{S9}$$

$$G_{trans} = -kT \ln \left[\left(\frac{2\pi M k T}{h^2} \right)^{3/2} V \right] \tag{S10}$$

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

$$\theta_i = \frac{h^2}{8\pi^2 I_i k} \tag{S12}$$

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}, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values at 593 K for C–C activations of ethane, propane, and butane via activations of α- and α,β-bound intermediates.

	y	γ	λ	R	R'		C	ΔH_{act} kJ mol^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ kJ mol^{-1}
RCH$_2$*–CH*R'‡	1	2	1.5	H	H	CH$_3$*–CH$_2$*‡	2	136	251	−67	291
				CH$_3$	H	CH$_3$CH$_2$*–CH$_2$*‡	3	147	261	−52	292
				H	CH$_3$	CH$_3$*–CH*CH$_3$‡	3	163	280	−45	306
				CH$_3$CH$_2$	H	CH$_3$CH$_2$CH$_2$*–CH$_2$*‡	4	150	257	−79	303
				H	CH$_3$CH$_2$	CH$_3$*–CH*CH$_2$CH$_3$‡	4	164	288	−48	316
				CH$_3$	CH$_3$	CH$_3$CH$_2$*–CH*CH$_3$‡	4	161	285	−66	324
RCH$_2$*–C*R'‡	2	2	2.0	H	H	CH$_3$*–CH*‡	2	95	231	5	229
				CH$_3$	H	CH$_3$CH$_2$*–CH*‡	3	100	235	−3	236
				H	CH$_3$	CH$_3$*–C*CH$_3$‡	3	99	249	−6	252
				CH$_3$CH$_2$	H	CH$_3$CH$_2$CH$_2$*–CH*‡	4	98	235	0	235
				H	CH$_3$CH$_2$	CH$_3$*–C*CH$_2$CH$_3$‡	4	104	224	−42	249
				CH$_3$	CH$_3$	CH$_3$CH$_2$*–C*CH$_3$‡	4	118	261	−22	274
RCH*–CH*R'‡	2	2	2.0	H	H	CH$_2$*–CH$_2$*‡	2	148	277	6	274
				CH$_3$	H	CH$_3$CH*–CH$_2$*‡	3	129	264	−3	266
				CH$_3$CH$_2$	H	CH$_3$CH$_2$CH*–CH$_2$*‡	4	117	254	−32	273
				CH$_3$	CH$_3$	CH$_3$CH*–CH*CH$_3$‡	4	117	261	−1	262
RCH$_2$*–C*‡	3	2	2.5	H	--	CH$_3$*–C*‡	2	202	281	73	238
				CH$_3$	--	CH$_3$CH$_2$*–C*‡	3	202	283	64	246
				CH$_3$CH$_2$	--	CH$_3$CH$_2$CH$_2$*–C*‡	4	203	284	61	248
RCH*–C*R'‡	3	2	2.5	H	H	CH$_2$*–CH*‡	2	108	259	64	221
				CH$_3$	H	CH$_3$CH*–CH*‡	3	82	233	54	201
				H	CH$_3$	CH$_2$*–C*CH$_3$‡	3	123	270	74	226
				CH$_3$CH$_2$	H	CH$_3$CH$_2$CH*–CH*‡	4	82	236	55	204
				H	CH$_3$CH$_2$	CH$_2$*–C*CH$_2$CH$_3$‡	4	123	273	68	233
				CH$_3$	CH$_3$	CH$_3$CH*–C*CH$_3$‡	4	94	246	51	216
RCH*–C*‡	4	2	3.0	H	--	CH$_2$*–C*‡	2	211	358	133	279
				CH$_3$	--	CH$_3$CH*–C*‡	3	185	321	125	247
				CH$_3$CH$_2$	--	CH$_3$CH$_2$CH*–C*‡	4	185	321	125	247
RC*–C*R'‡	4	2	3.0	H	H	CH*–CH*‡	2	62	218	136	137
				CH$_3$	H	CH$_3$C*–CH*‡	3	67	207	125	139
				CH$_3$CH$_2$	H	CH$_3$CH$_2$C*–CH*‡	4	70	210	111	144
				CH$_3$	CH$_3$	CH$_3$C*–CCH$_3$*‡	4	83	215	113	148
RC*–C*‡	5	2	3.5	H	--	CH*–C*‡	2	93	340	184	231
				CH$_3$	--	CH$_3$C*–C*‡	3	89	313	192	199
				CH$_3$CH$_2$	--	CH$_3$CH$_2$C*–C*‡	4	98	321	175	218

Table S2. ΔH_{act}, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values at 593 K for C–C activations of propane and butane via $RCH_x{}^*CH_x{}^*–R'^{\ddagger}$ (x = 0-1) transition states.

	y	γ	λ	R	R'		C	ΔH_{act} kJ mol⁻¹	$\Delta H^{\ddagger}$ kJ mol⁻¹	$\Delta S^{\ddagger}$ J mol⁻¹ K⁻¹	$\Delta G^{\ddagger}$ kJ mol⁻¹
RCH*CH*–R'*‡	2	3	2.5	H	CH₃	CH₂*CH*–CH₃*‡	3	143	293	10	287
				H	CH₃CH₂	CH₂*CH*–CH₂*CH₃‡	4	152	308	11	301
RCH*C*–R'*‡	3	3	3.0	H	CH₃	CH₂*C*–CH₃*‡	3	235	334	60	299
				H	CH₃CH₂	CH₂*C*–CH₂*CH₃‡	4	120	288	73	245
RC*–CH*R'‡	3	3	3.0	H	CH₃	CH*CH*–CH₃*‡	3	138	306	51	275
				H	CH₃CH₂	CH*CH*–CH₂*CH₃‡	4	155	325	83	276
RC*–C*R'‡	4	3	3.5	H	CH₃	CH*C*–CH₃*‡	3	200	361	147	274
				H	CH₃CH₂	CH*C*–CH₂*CH₃‡	4	198	364	139	281

Table S3. ΔH_{act}, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values at 593 K for C–C activations of propane and butane in α,γ-bound intermediates.

	y	ℓ	λ	R	R'		C	ΔH_{act} kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ kJ mol^{-1}
RCH*CH$_2$–CH(R')*‡	2	2^a	2.0	H	H	*CH$_2$CH$_2$–CH$_2$*	3	171	319	1	318
				CH$_3$	H	CH$_3$CH*CH$_2$–CH$_2$*	4	142	296	0	296
				H	CH$_3$	*CH$_2$CH$_2$–CH*CH$_3$	4	161	316	11	309
RC*CH$_2$*–CH(R')*‡	3	3	3.0	H	H	*CHCH$_2$*–CH$_2$*	3	134	327	64	290
				CH$_3$	H	CH$_3$C*CH$_2$–CH$_2$*	4	123	315	43	289
				H	CH$_3$	*CHCH$_2$*–CH*CH$_3$	4	134	335	55	302
RCH*CH$_2$–CR'*‡	3	2^a	2.5	H	H	*CH$_2$CH$_2$–CH*	3	106	282	62	246
				CH$_3$	H	CH$_3$CH*CH$_2$–CH*	4	113	297	57	264
				H	CH$_3$	*CH$_2$CH$_2$–C*CH$_3$	4	112	303	38	281
C*CH$_2$*–CH(R')*‡	4	3	3.5	H	H	*CCH$_2$*–CH$_2$*	3	128	312	128	237
				H	CH$_3$	*CCH$_2$*–CH*CH$_3$	4	113	326	124	252
RCH*CH$_2$–C*‡	4	2^a	3.0	H		*CH$_2$CH$_2$–C*	3	170	337	128	261
				CH$_3$		CH$_3$CH*CH$_2$–C*	4	107	275	113	208
RC*CH$_2$*–CR'*‡	4	3	3.5	H	H	*CHCH$_2$*–CH*	3	67	309	120	238
				CH$_3$	H	CH$_3$C*CH$_2$*–CH*	4	63	313	119	243
				H	CH$_3$	*CHCH$_2$*–C*CH$_3$	4	71	320	118	250
C*CH$_2$*–CR'*‡	5	3	4.0		H	*CCH$_2$*–CH*	3	62	318	187	207
					CH$_3$	*CCH$_2$*–C*CH$_3$	4	66	325	184	216
RC*CH$_2$*–C*‡	5	3	4.0	H		*CHCH$_2$*–C*	3	136	391	189	279
				CH$_3$		CH$_3$C*CH$_2$*–C*	4	150	408	189	296
C*CH$_2$*–C*‡	6	3	4.5			*CCH$_2$*–C*	3	46	372	251	223

^{a} Concerted alkene (g) formation reduces the site requirements as the ^{2}C-atoms do not ever bind to the catalyst surface.

Table S4. ΔH_{act}, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values at 593 K for C–C activations of propane and isobutane in α,β,γ-bound intermediates.

	y	ℓ	λ	R	R'		C	ΔH_{act} kJ mol^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$ J mol^{-1} K^{-1}	$\Delta G^{\ddagger}$ kJ mol^{-1}
RCH*CH*–CH*R'	3	3	3.0	H	H	CH_2*CH*–CH_2*	3	138	301	63	264
				CH_3	H	CH_3CH*CH*–CH_2*	4	131	298	64	260
				H	CH_3	CH_2*CH*–CH*CH_3	4	142	303	60	268
RCH*C*–CH*R'	4	3	3.0	H	H	CH_2*C*–CH_2*	3	86	304	126	230
				CH_3	H	CH_3CH*C*–CH_2*	4	81	299	126	225
				H	CH_3	CH_2*C*–CH*CH_3	4	109	325	151	236
RC*CH*–CH*R'	4	3	3.5	H	H	CH*CH*–CH_2*	3	94	302	119	231
				CH_3	H	CH_3C*CH*–CH_2*	4	93	297	122	225
				H	CH_3	CH*CH*–CH*CH_3	4	101	311	121	240
RC*C*–CH*R'	5	3	4.0	H	H	CH*C*–CH_2*	3	180	396	199	278
				CH_3	H	CH_3C*C*–CH_2*	4	174	377	205	255
				H	CH_3	CH*C*–CH*CH_3	4	150	368	202	248
RCH*CH*–C*R'	4	3	3.5	H	H	CH_2*CH*–CH*	3	111	319	121	248
				CH_3	H	CH_3CH*CH*–CH*	4	111	321	119	251
				H	CH_3	CH_2*CH*–C*CH_3	4	104	308	127	233
RCH*C*–C*R'	5	3	4.0	H	H	CH_2*C*–CH*	3	87	303	185	193
				CH_3	H	CH_3CH*C*–CH*	4	77	295	190	182
				H	CH_3	CH_2*C*–C*CH_3	4	92	294	196	178
C*CH*–CH*R'	5	3	4.0	H	H	C*CH*–CH_2*	3	164	375	218	246
				H	CH_3	C*CH*–CH*CH_3	4	150	369	205	247
C*C*–CH*R'	6	3	4.5	H	H	C*C*–CH_2*	3	207	505	263	349
				H	CH_3	C*C*–CH*CH_3	4	205	500	248	353
RCH*CH*–C*	5	3	4.0	H		CH_2*CH*–C*	3	199	410	189	298
				CH_3		CH_3CH*CH*–C*	4	170	382	191	269
RCH*C*–C*	6	3	4.5	H		CH_2*C*–C*	3	140	439	261	284
				CH_3		CH_3CH*C*–C*	4	133	429	263	273
RC*CH*–C*R'	5	3	4.0	H	H	CH*CH*–CH*	3	82	339	189	227
				CH_3	H	CH_3C*CH*–CH*	4	79	328	195	213
				H	CH_3	CH*CH*–C*CH_3	4	81	330	192	216
RC*C*–C*R'	5	3	4.0	H	H	CH*C*–CH*	3	116	393	253	243
				CH_3	H	CH_3C*C*–CH*	4	117	376	257	223
				H	CH_3	CH*C*–C*CH_3	4	127	381	253	231
C*CH*–C*R'	6	3	4.5		H	C*CH*–CH*	3	117	377	255	226
					CH_3	C*CH*–C*CH_3	4	123	383	257	230
C*C*–C*R'	7	3	5.0		H	C*C*–CH*	3	132	509	324	317
					CH_3	C*C*–C*CH_3	4	135	493	310	309
RC*CH*–C*	6	3	4.5	H		CH*CH*–C*	3	167	427	251	279
				CH_3		CH_3C*CH*–C*	4	163	417	254	267
RC*C*–C*	7	3	5.0	H		CH*C*–C*	3	159	536	322	344
				CH_3		CH_3C*C*–C*	4	154	512	330	316
C*CH*–C*	7	3	5.0			*CCH*–C*	3	123	485	328	291
C*C*–C*	8	3	5.5			*CC*–C*	3	109	624	392	391

Table S5. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values at 593 K for C–C activations of butane in α,β,δ-bound intermediates.

y	ℓ	λ	α,β,δ-bound Intermediate	Transition State	ΔH_{act} kJ mol^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$ J mol^{-1} K^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}
3	3	3.0	CH$_2$*CH$_2$CH*CH$_2$*	CH$_2$*CH$_2$–CH*CH$_2$*$\neq$	158	357	79	310
4	3	3.5	CH$_2$*CH$_2$CH*CH*	CH$_2$*CH$_2$CH*–CH*$\neq$	78	337	130	260
4	3	3.5	CH$_2$*CH$_2$CH*CH*	CH$_2$*CH$_2$–CH*CH*$\neq$	102	344	110	279
4	3	3.5	CH$_2$*CH$_2$C*CH$_2$*	CH$_2$*CH$_2$–C*CH$_2$*$\neq$	112	317	137	236
4	4	4.0	CH$_2$*CH*CH$_2$CH*	CH$_2$*CH*–CH$_2$*CH*$\neq$	130	366	124	293
5	3	4.0	CH$_2$*CH$_2$CH*C*	CH$_2$*CH$_2$–CH*C*$\neq$	193	423	188	312
5	4	4.5	CH$_2$*CH*CH$_2$C*	CH$_2$*CH*–CH$_2$*C*$\neq$	96	364	206	242
5	4	4.5	CH$_2$*C*CH$_2$CH*	CH$_2$*C*–CH$_2$*CH*$\neq$	58	343	190	230
5	4	4.5	CH*CH$_2$CH*CH*	CH*CH$_2$*–CH*CH*$\neq$	89	363	186	252
5	3	4.0	CH*CH$_2$CH*CH*	CH*CH$_2$CH*–CH*$\neq$	85	358	188	247
6	4	5.0	CH$_2$*C*CH$_2$C*	CH$_2$*C*–CH$_2$*C*$\neq$	55	350	261	195
6	4	5.0	CH*CH$_2$CH*C*	CH*CH$_2$*–CH*C*$\neq$	194	458	256	306
6	4	5.0	CH*CH$_2$CH*C*	CH*–CH$_2$*CH*C*$\neq$	180	444	261	290
6	4	5.0	CH*CH$_2$C*CH*	CH*–CH$_2$*C*CH*$\neq$	145	409	236	269
6	4	5.0	CH*CH*CH$_2$C*	CH*CH*–CH$_2$*C*$\neq$	91	358	269	198
6	3	4.5	CH*CH*CH$_2$C*	CH*–CH*CH$_2$C*$\neq$	106	389	235	249
7	4	5.5	CH*C*CH$_2$C*	CH*C*–CH$_2$*C*$\neq$	133	451	339	250
7	4	5.5	C*CH$_2$CH*C*	C*CH$_2$*–CH*C*$\neq$	140	423	335	224

Table S6. ΔH_{act}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values at 593 K for C–C activations of butane in $\alpha,\beta,\gamma,\delta$-bound intermediates.

y	ℓ	λ	$\alpha,\beta,\gamma,\delta$-bound Intermediate	Transition State	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$_2$*CH*CH*CH$_2$*	CH$_2$*CH*–CH*CH$_2$*$\neq$	129	350	135	270
5	4	4.5	CH$_2$*CH*CH*CH*	CH$_2$*CH*–CH*CH*$\neq$	125	352	196	236
5	4	4.5	CH$_2$*CH*C*CH$_2$*	CH$_2$*CH*–C*CH$_2$*$\neq$	135	353	199	235
6	4	5.0	CH$_2$*CH*CH*C*	CH$_2$*CH*–CH*C*$\neq$	168	426	260	272
6	4	5.0	CH$_2$*CH*C*CH*	CH$_2$*CH*–C*CH*$\neq$	84	363	268	204
6	4	5.0	CH$_2$*C*CH*CH*	CH$_2$*C*CH*–CH*$\neq$	148	410	257	258
6	4	5.0	CH$_2$*C*CH*CH*	CH$_2$*C*–CH*CH*$\neq$	95	357	262	202
6	4	5.0	CH$_2$*C*C*CH$_2$*	CH$_2$*C*–C*CH$_2$*$\neq$	81	373	264	216
6	4	5.0	CH*CH*CH*CH*	CH*CH*–CH*CH*$\neq$	112	379	250	230
7	4	5.5	CH$_2$*C*CH*C*	CH$_2$*C*–CH*C*$\neq$	132	427	331	231
7	4	5.5	CH$_2$*C*C*CH*	CH$_2$*C*C*–CH*$\neq$	131	460	328	265
7	4	5.5	CH*CH*CH*C*	CH*CH*–CH*C*$\neq$	182	490	323	298
7	4	5.5	CH*CH*CH*C*	CH*–CH*CH*C*$\neq$	72	380	316	192
7	4	5.5	CH*CH*C*CH*	CH*CH*–C*CH*$\neq$	89	493	326	299
7	4	5.5	CH*CH*C*CH*	CH*CH*C*–CH*$\neq$	67	436	320	246
8	4	6.0	C*CH*CH*C*	C*CH*–CH*C*$\neq$	195	503	398	268
10	4	7.0	C*C*C*C*	C*C*–C*C*$\neq$	151	797	558	467