Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information for

Pathways for C-H bond cleavage of propane σ-complexes on PdO(101)

Abbin Antony[a], Aravind Asthagiri[b] and Jason F. Weaver[a]*

[a]Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

[b]William G. Lowrie Department of Chemical & Biomolecular Engineering, The Ohio State University, Columbus, OH 43210, USA

Table 1 summarizes the DFT-D3 binding energies of different propane states on the PdO(101) surface and the corresponding zero point corrected energies and activation barriers assuming 3*N* and 3*N*-2 harmonic modes for the adsorbed structures. Zero point energies are evaluated by employing the vibrational mode frequencies in Equation (i) where the number of modes for chemisorbed propane is 3*N* if all are treated harmonic, 3*N*-2 if two modes are treated free and 3N-6 for isolated propane (gas). Based on the definition of binding energy in the section titled "Computational Details, (Equation (2))", the zero point corrected binding energy is evaluated as shown in Equation (ii).

$$ZPE = \sum_{j=1}^{\#\ Harmonic\ modes} \frac{1}{2} hc\nu_j \qquad \text{(i)}$$

$$E\ (ZPC) = E - ZPE_{chemisorb} + ZPE_{iso} \qquad \text{(ii)}$$

				3*N* Harmonic modes		3*N*-2 Harmonic modes	
	State	$\Delta E_{d,i}^{\neq}$ (kJ/mol)	$\Delta E_{r,i}^{\neq}$ (kJ/mol)	$\Delta E_{d,i}^{\neq}$ (ZPC) (kJ/mol)	$\Delta E_{r,i}^{\neq}$ (ZPC) (kJ/mol)	$\Delta E_{d,i}^{\neq}$ (ZPC) (kJ/mol)	$\Delta E_{r,i}^{\neq}$ (ZPC) (kJ/mol)
p-η^2(+)		59.1		58.9			
s-η^2		69.1		69.5		69.9	
p-η^2(-)		57.3		57.0			
p-2η^1(st)	IS	71.9		70.5		71.1	
	TS	6.0	65.9	18.7	51.8	19.5	51.6
	FS	114.3		112.2			
p-2η^1(fl)	IS	70.5		67.5		68.3	
	TS	2.3	68.2	14.7	52.8	15.7	52.6
	FS	113.4		111.2			
s-η^1(st)	IS	62.0		63.1		64.2	
	TS	-4.2	66.1	9.0	54.1	10.5	53.7
	FS	114.2		112.6			
s-η^1(fl)	IS	64.0		66.1		66.8	
	TS	-8.3	72.3	5.1	61.0	6.5	60.3
	FS	105.6		104.5			

Table 1: Binding energies, zero point corrected binding energies evaluated by treating 3*N* and 3*N*-2 modes harmonics and corresponding energy barriers for C-H bond cleavage.

Tables 2 through 4 list the normal mode vibrational frequencies computed for isolated and chemisorbed propane molecules on PdO(101) using DFT-D3. The highlighted modes in the table are imaginary modes which are observed due to the relatively flat potential energy surface about the cus Pd atom. This feature of the potential energy surface results in configurations relaxing onto another saddle point when performing imaginary mode calculations (*imc*) where the configuration is pushed along the imaginary mode. Binding energies, geometries and vibrational modes of the newly relaxed configurations are very similar to the configurations prior to *imc*. Vibrational modes identified as free motions for microkinetic analysis have been tagged as '(fm)'.

Isolated C_3H_8			p-η^2(+)	s-η^2	p-η^2(-)
Mode No.	ν_j (cm^{-1})	*Mode No.*	ν_j (cm^{-1})	ν_j (cm^{-1})	ν_j (cm^{-1})
1	3043	1	3058	3070	3083
2	3041	2	3052	3053	3050
3	3038	3	3050	3048	3035
4	3028	4	3000	3045	2999
5	2986	5	2982	2981	2971
6	2965	6	2965	2975	2962
7	2963	7	2857	2858	2934
8	2960	8	2629	2473	2583
9	1458	9	1466	1485	1452
10	1452	10	1447	1456	1444
11	1440	11	1441	1436.	1432
12	1437	12	1429	1435	1426
13	1431	13	1401	1424	1405
14	1364	14	1372	1364	1365
15	1350	15	1310	1343	1310
16	1316	16	1276	1257	1277
17	1275	17	1268	1186	1266
18	1164	18	1171	1163	1175
19	1136	19	1116	1140	1121
20	1051	20	1055	1044	1057
21	897	21	915	900	930
22	882	22	895	879	891
23	864	23	858	869	861
24	719	24	742	81	741
25	355	25	389	370	382
26	261	26	299	256	28
27	196	27	244	182	240
		28	163	153	137
		29	113	137	107
		30	50	78	71
		31	43	71	63
		32	21*i*	42 (fm)	18*i*
		33	37*i*	16*i* (fm)	45*i*

Table 2: Vibrational mode frequencies of isolated propane molecule and propane in p-η^2(+),s-η^2 and p-η^2(-) configurations.

p-2η^1(*st*)				p-2η^1(*fl*)			
	ν_j (cm^{-1})				ν_j (cm^{-1})		
Mode No.	*IS*	*TS*	*FS*	*Mode No.*	*IS*	*TS*	*FS*
1	3064	3051	3600	1	3079	3073	3578
2	3062	3018	3062	2	3076	3013	3063
3	3021	3004	3009	3	3028	2992	3009
4	3011	2993	3005	4	3022	2963	2980
5	3001	2973	2964	5	3013	2932	2933
6	2964	2944	2949	6	2977	2901	2914
7	2762	2661	2925	7	2763	2788	2896
8	2748	1615	2685	8	2749	1607	2813
9	1444	1432	1421	9	1485	1427	1421
10	1433	1420	1410	10	1474	1418	1398
11	1432	1388	1388	11	1438	1390	1384
12	1414	1368	1366	12	1425	1337	1373
13	1414	1323	1327	13	1418	1329	1327
14	1319	1282	1291	14	1321	1299	1294
15	1306	1235	1228	15	1308	1238	1230
16	1284	1188	1155	16	1286	1187	1159
17	1254	1137	1098	17	1253	1154	1114
18	1183	1069	1067	18	1188	1080	1072
19	1101	1017	951	19	1104	1029	960
20	1067	959	946	20	1068	963	950
21	931	877	867	21	940	900	869
22	872	863	814	22	876	865	812
23	864	739	751	23	870	744	749
24	743	619	683	24	765	589	694
25	374	426	676	25	388	454	681
26	364	404	478	26	386	411	469
27	350	349	388	27	360	336	397
28	178	205	314	28	176	227	329
29	129	152	229	29	132	141	221
30	71	113	133	30	94 (fm)	85 (fm)	146
31	70 (fm)	68 (fm)	99	31	57	79 (fm)	90
32	44	65 (fm)	78	32	35 (fm)	40	71
33	38 (fm)	1323*i*	63	33	17	1297*i*	47

Table 3: Vibrational mode frequencies of propane in p-2η^1(*st*) and p-2η^1(fl) configurations.

s-$\eta^1(st)$				s-$\eta^1(fl)$			
	ν_j (cm^{-1})				ν_j (cm^{-1})		
Mode No.	*IS*	*TS*	*FS*	*Mode No.*	*IS*	*TS*	*FS*
1	3058	3049	3599	1	3050	2999	3547
2	3052	3048	3022	2	3047	2997	2989
3	3038	2988	3018	3	3040	2987	2984
4	3018	2986	2965	4	3029	2964	2979
5	3010	2983	2962	5	3016	2925	2954
6	2972	2910	2958	6	2976	2887	2920
7	2950	2907	2906	7	2958	2843	2892
8	2545	1644	2905	8	2595	1611	2883
9	1444	1429	1426	9	1444	1433	1415
10	1434	1420	1417	10	1440	1423	1412
11	1422	1415	1413	11	1427	1416	1402
12	1420	1399	1393	12	1421	1397	1391
13	1411	1353	1351	13	1362	1354	1342
14	1360	1333	1336	14	1348	1339	1329
15	1341	1265	1284	15	1305	1261	1273
16	1294	1162	1148	16	1291	1153	1189
17	1196	1105	1090	17	1147	1124	1102
18	1149	1097.	1090	18	1145	1098	1095
19	1134	1013	931	19	1134	989	959
20	1030	943	908	20	1026	964	907
21	895	923	880	21	901	903	876
22	882	874	863	22	871	884	868
23	844	846	807	23	830	866	803
24	812	433	679	24	695	467	711
25	359	347	491	25	363	372	473
26	273	233	396	26	267	262	393
27	175	203	243	27	214	245	254
28	141 (fm)	184	233	28	131	222	232
29	75	179 (fm)	221	29	84 (fm)	205 (fm)	221
30	62	94	218.	30	43	121	219
31	28	72 (fm)	95	31	32 (fm)	89	130
32	14	37*i*	63	32	18	34 (fm)	90
33	43*i* (fm)	1355*i*	29	33	51*i*	1213*i*	23

Table 4: Vibrational mode frequencies of propane in s-$\eta^1(st)$ and s-$\eta^1(fl)$ configurations.