

Microkinetic Mechanisms for Partial Oxidation of Methane over Platinum and Rhodium

Supporting Information

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Table S1: Comparison of activation barriers of Filot et al. [40] with the UBI-QEP determinations for the "hybrid" and VTST mechanisms for Rh. Values in kJ/mol.

Reaction	Filot et al.	UBI-QEP
$C_2H_6(s)_2 \rightarrow H(s) + CH_2CH_3(s)$	34	8
$H(s) + CH_2CH_3(s) \rightarrow C_2H_6(s)_2$	91	49
$CH_2CH_3(s) + 2(s) \rightarrow H(s) + C_2H_4(s)_2$	65	0
$H(s) + C_2H_4(s)_2 \rightarrow CH_2CH_3(s) + 2(s)$	58	96
$H(s) + C_2H_4(s) \rightarrow CH_2CH_3(s) + (s)$	58	91
$CH_2CH_3(s) + (s) \rightarrow H(s) + C_2H_4(s)$	65	0
$C_2H_4(s) + (s) \rightarrow H(s) + CHCH_2(s)$	35	27
$H(s) + CHCH_2(s) \rightarrow C_2H_4(s) + (s)$	66	36
$C_2H_4(s) + 3(s) \rightarrow CHCH_2(s)_3 + H(s)$	35	27
$CHCH_2(s)_3 + H(s) \rightarrow C_2H_4(s) + 3(s)$	66	37
$C_2H_4(s)_2 \rightarrow H(s) + CHCH_2(s)$	35	31
$H(s) + CHCH_2(s) \rightarrow C_2H_4(s)_2$	66	33
$H(s) + CHCH_3(s)_2 \rightarrow CH_2CH_3(s) + 2(s)$	71	58
$CH_2CH_3(s) + 2(s) \rightarrow H(s) + CHCH_3(s)_2$	30	49
$CHCH_3(s)_2 + 2(s) \rightarrow CHCH_2(s)_3 + H(s)$	92	0
$CHCH_2(s)_3 + H(s) \rightarrow CHCH_3(s)_2 + 2(s)$	89	110
$CHCH_3(s)_2 + 2(s) \rightarrow H(s) + CCH_3(s)_3$	53	19
$H(s) + CCH_3(s)_3 \rightarrow CHCH_3(s)_2 + 2(s)$	102	115
$CHCH_3(s)_2 \rightarrow CHCH_2(s) + H(s)$	92	0
$CHCH_2(s) + H(s) \rightarrow CHCH_3(s)_2$	89	109
$CHCH_2(s) + 2(s) \rightarrow CCH_2(s)_2 + H(s)$	18	0
$CCH_2(s)_2 + H(s) \rightarrow CHCH_2(s) + 2(s)$	111	135
$CHCH_2(s) + 3(s) \rightarrow C_2H_2(s)_3 + H(s)$	35	0

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Reaction	Filot et al.	UBI-QEP
$C_2H_2(s)_3 + H(s) \rightarrow CHCH_2(s) + 3 (s)$	101	106
$CCH_3(s)_3 + (s) \rightarrow C(s)_3 + CH_3(s)$	144	2
$C(s)_3 + CH_3(s) \rightarrow CCH_3(s)_3 + (s)$	119	56
$CCH_2(s)_2 + H(s) \rightarrow CCH_3(s)_3$	80	162
$CCH_3(s)_3 \rightarrow CCH_2(s)_2 + H(s)$	40	0
$CCH_2(s)_2 \rightarrow H(s) + CCH(s)$	75	77
$H(s) + CCH(s) \rightarrow CCH_2(s)_2$	44	17
$CCH_2(s)_3 + H(s) \rightarrow CHCH_2(s)_3 + (s)$	111	315
$CHCH_2(s)_3 + (s) \rightarrow CCH_2(s)_3 + H(s)$	18	0
$CCH_2(s)_3 + H(s) \rightarrow CCH_3(s)_3 + (s)$	80	342
$CCH_3(s)_3 + (s) \rightarrow CCH_2(s)_3 + H(s)$	40	0
$H(s) + C_2H_2(s)_3 \rightarrow CHCH_2(s)_3 + (s)$	101	106
$CHCH_2(s)_3 + (s) \rightarrow H(s) + C_2H_2(s)_3$	35	0
$H(s) + CCH(s) + (s) \rightarrow CCH_2(s)_3$	75	0
$CCH_2(s)_3 \rightarrow H(s) + CCH(s) + (s)$	44	230
$CCH(s) + H(s) + (s) \rightarrow C_2H_2(s)_3$	160	0
$C_2H_2(s)_3 \rightarrow CCH(s) + H(s) + (s)$	102	85
$CCH(s) + 5 (s) \rightarrow C(s)_3 + CH(s)_3$	93	85
$C(s)_3 + CH(s)_3 \rightarrow CCH(s) + 5 (s)$	103	89
$CH_3(s) + H(s) \rightarrow CH_4 + 2 (s)$	50	19
$CH_4 + 2 (s) \rightarrow CH_3(s) + H(s)$	36	20
$CH_3(s) + O(s) \rightarrow CH_3O(s) + (s)$	199	0
$CH_3O(s) + (s) \rightarrow CH_3(s) + O(s)$	112	77

Table S1: Comparison of activation barriers of Filot et al. [40] with the UBI-QEP determinations for the "hybrid" and VTST mechanisms for Rh. Values in kJ/mol.

Reaction	Filot et al.	UBI-QEP
$\text{CH}_3(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{CH}_3\text{OH}(\text{s}) + (\text{s})$	173	0
$\text{CH}_3\text{OH}(\text{s}) + (\text{s}) \rightarrow \text{CH}_3(\text{s}) + \text{OH}(\text{s})$	94	148
$\text{CH}_2(\text{s})_2 + \text{H}(\text{s}) \rightarrow \text{CH}_3(\text{s}) + 2 (\text{s})$	33	57
$\text{CH}_3(\text{s}) + 2 (\text{s}) \rightarrow \text{CH}_2(\text{s})_2 + \text{H}(\text{s})$	15	47
$\text{CH}_2(\text{s})_2 + \text{OH}(\text{s}) \rightarrow \text{CH}_2\text{OH}(\text{s}) + 2 (\text{s})$	118	0
$\text{CH}_2\text{OH}(\text{s}) + 2 (\text{s}) \rightarrow \text{CH}_2(\text{s})_2 + \text{OH}(\text{s})$	57	102
$\text{H}(\text{s}) + \text{CH}(\text{s})_3 \rightarrow \text{CH}_2(\text{s})_2 + 2 (\text{s})$	78	112
$\text{CH}_2(\text{s})_2 + 2 (\text{s}) \rightarrow \text{H}(\text{s}) + \text{CH}(\text{s})_3$	23	33
$\text{H}(\text{s}) + \text{C}(\text{s})_3 \rightarrow \text{CH}(\text{s})_3 + (\text{s})$	80	260
$\text{CH}(\text{s})_3 + (\text{s}) \rightarrow \text{H}(\text{s}) + \text{C}(\text{s})_3$	91	0
$\text{C}(\text{s})_3 + \text{O}(\text{s}) \rightarrow \text{CO}(\text{s})_2 + 2 (\text{s})$	92	60
$\text{CO}(\text{s})_2 + 2 (\text{s}) \rightarrow \text{C}(\text{s})_3 + \text{O}(\text{s})$	173	214
$\text{CO}(\text{s})_2 + \text{O}(\text{s}) \rightarrow \text{CO}_2(\text{s})_2 + (\text{s})$	80	79
$\text{CO}_2(\text{s})_2 + (\text{s}) \rightarrow \text{CO}(\text{s})_2 + \text{O}(\text{s})$	136	30
$\text{CH}_3\text{O}(\text{s}) + \text{H}(\text{s}) \rightarrow \text{CH}_3\text{OH}(\text{s}) + (\text{s})$	60	96
$\text{CH}_3\text{OH}(\text{s}) + (\text{s}) \rightarrow \text{CH}_3\text{O}(\text{s}) + \text{H}(\text{s})$	55	53
$\text{CH}_3\text{O}(\text{s}) + (\text{s}) \rightarrow \text{H}(\text{s}) + \text{CH}_2\text{O}(\text{s})$	72	0
$\text{H}(\text{s}) + \text{CH}_2\text{O}(\text{s}) \rightarrow \text{CH}_3\text{O}(\text{s}) + (\text{s})$	146	218
$\text{CH}_2\text{OH}(\text{s}) + \text{H}(\text{s}) \rightarrow \text{CH}_3\text{OH}(\text{s}) + (\text{s})$	183	0
$\text{CH}_3\text{OH}(\text{s}) + (\text{s}) \rightarrow \text{CH}_2\text{OH}(\text{s}) + \text{H}(\text{s})$	147	89
$\text{CH}_2\text{OH}(\text{s}) + 2 (\text{s}) \rightarrow \text{CHOH}(\text{s})_2 + \text{H}(\text{s})$	15	2
$\text{CHOH}(\text{s})_2 + \text{H}(\text{s}) \rightarrow \text{CH}_2\text{OH}(\text{s}) + 2 (\text{s})$	63	61
$\text{CH}_2\text{OH}(\text{s}) + (\text{s}) \rightarrow \text{H}(\text{s}) + \text{CH}_2\text{O}(\text{s})$	69	0

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Reaction	Filot et al.	UBI-QEP
$\text{H(s)} + \text{CH}_2\text{O(s)} \rightarrow \text{CH}_2\text{OH(s)} + (\text{s})$	112	302
$\text{CH}_2\text{O(s)} + (\text{s}) \rightarrow \text{H(s)} + \text{CHO(s)}$	14	129
$\text{H(s)} + \text{CHO(s)} \rightarrow \text{CH}_2\text{O(s)} + (\text{s})$	69	0
$\text{CHOH(s)}_2 + 2 (\text{s}) \rightarrow \text{COH(s)}_3 + \text{H(s)}$	50	0
$\text{COH(s)}_3 + \text{H(s)} \rightarrow \text{CHOH(s)}_2 + 2 (\text{s})$	109	178
$\text{CHOH(s)}_2 \rightarrow \text{CHO(s)} + \text{H(s)}$	109	0
$\text{CHO(s)} + \text{H(s)} \rightarrow \text{CHOH(s)}_2$	159	141
$\text{CHO(s)} + 2 (\text{s}) \rightarrow \text{H(s)} + \text{CO(s)}_2$	17	0
$\text{H(s)} + \text{CO(s)}_2 \rightarrow \text{CHO(s)} + 2 (\text{s})$	120	244
$\text{COH(s)}_3 \rightarrow \text{CO(s)}_2 + \text{H(s)}$	68	0
$\text{CO(s)}_2 + \text{H(s)} \rightarrow \text{COH(s)}_3$	161	183
$\text{O(s)} + \text{H}_2\text{O(s)} \rightarrow \text{OH(s)} + \text{OH(s)}$	53	155
$\text{OH(s)} + \text{OH(s)} \rightarrow \text{O(s)} + \text{H}_2\text{O(s)}$	53	0
$\text{H(s)} + \text{O(s)} \rightarrow \text{OH(s)} + (\text{s})$	156	185
$\text{OH(s)} + (\text{s}) \rightarrow \text{H(s)} + \text{O(s)}$	142	5
$\text{H(s)} + \text{OH(s)} \rightarrow \text{H}_2\text{O(s)} + (\text{s})$	108	60
$\text{H}_2\text{O(s)} + (\text{s}) \rightarrow \text{H(s)} + \text{OH(s)}$	77	85