# 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 |
|---|---|---|
| $CH_3(s) + OH(s) \rightarrow CH_3OH(s) + (s)$ | 173 | 0 |
| $CH_3OH(s) + (s) \rightarrow CH_3(s) + OH(s)$ | 94 | 148 |
| $CH_2(s)_2 + H(s) \rightarrow CH_3(s) + 2\ (s)$ | 33 | 57 |
| $CH_3(s) + 2\ (s) \rightarrow CH_2(s)_2 + H(s)$ | 15 | 47 |
| $CH_2(s)_2 + OH(s) \rightarrow CH_2OH(s) + 2\ (s)$ | 118 | 0 |
| $CH_2OH(s) + 2\ (s) \rightarrow CH_2(s)_2 + OH(s)$ | 57 | 102 |
| $H(s) + CH(s)_3 \rightarrow CH_2(s)_2 + 2\ (s)$ | 78 | 112 |
| $CH_2(s)_2 + 2\ (s) \rightarrow H(s) + CH(s)_3$ | 23 | 33 |
| $H(s) + C(s)_3 \rightarrow CH(s)_3 + (s)$ | 80 | 260 |
| $CH(s)_3 + (s) \rightarrow H(s) + C(s)_3$ | 91 | 0 |
| $C(s)_3 + O(s) \rightarrow CO(s)_2 + 2\ (s)$ | 92 | 60 |
| $CO(s)_2 + 2\ (s) \rightarrow C(s)_3 + O(s)$ | 173 | 214 |
| $CO(s)_2 + O(s) \rightarrow CO_2(s)_2 + (s)$ | 80 | 79 |
| $CO_2(s)_2 + (s) \rightarrow CO(s)_2 + O(s)$ | 136 | 30 |
| $CH_3O(s) + H(s) \rightarrow CH_3OH(s) + (s)$ | 60 | 96 |
| $CH_3OH(s) + (s) \rightarrow CH_3O(s) + H(s)$ | 55 | 53 |
| $CH_3O(s) + (s) \rightarrow H(s) + CH_2O(s)$ | 72 | 0 |
| $H(s) + CH_2O(s) \rightarrow CH_3O(s) + (s)$ | 146 | 218 |
| $CH_2OH(s) + H(s) \rightarrow CH_3OH(s) + (s)$ | 183 | 0 |
| $CH_3OH(s) + (s) \rightarrow CH_2OH(s) + H(s)$ | 147 | 89 |
| $CH_2OH(s) + 2\ (s) \rightarrow CHOH(s)_2 + H(s)$ | 15 | 2 |
| $CHOH(s)_2 + H(s) \rightarrow CH_2OH(s) + 2\ (s)$ | 63 | 61 |
| $CH_2OH(s) + (s) \rightarrow H(s) + CH_2O(s)$ | 69 | 0 |

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| Reaction | Filot et al. | UBI–QEP |
|---|---|---|
| $H(s) + CH_2O(s) \rightarrow CH_2OH(s) + (s)$ | 112 | 302 |
| $CH_2O(s) + (s) \rightarrow H(s) + CHO(s)$ | 14 | 129 |
| $H(s) + CHO(s) \rightarrow CH_2O(s) + (s)$ | 69 | 0 |
| $CHOH(s)_2 + 2\ (s) \rightarrow COH(s)_3 + H(s)$ | 50 | 0 |
| $COH(s)_3 + H(s) \rightarrow CHOH(s)_2 + 2\ (s)$ | 109 | 178 |
| $CHOH(s)_2 \rightarrow CHO(s) + H(s)$ | 109 | 0 |
| $CHO(s) + H(s) \rightarrow CHOH(s)_2$ | 159 | 141 |
| $CHO(s) + 2\ (s) \rightarrow H(s) + CO(s)_2$ | 17 | 0 |
| $H(s) + CO(s)_2 \rightarrow CHO(s) + 2\ (s)$ | 120 | 244 |
| $COH(s)_3 \rightarrow CO(s)_2 + H(s)$ | 68 | 0 |
| $CO(s)_2 + H(s) \rightarrow COH(s)_3$ | 161 | 183 |
| $O(s) + H_2O(s) \rightarrow OH(s) + OH(s)$ | 53 | 155 |
| $OH(s) + OH(s) \rightarrow O(s) + H_2O(s)$ | 53 | 0 |
| $H(s) + O(s) \rightarrow OH(s) + (s)$ | 156 | 185 |
| $OH(s) + (s) \rightarrow H(s) + O(s)$ | 142 | 5 |
| $H(s) + OH(s) \rightarrow H_2O(s) + (s)$ | 108 | 60 |
| $H_2O(s) + (s) \rightarrow H(s) + OH(s)$ | 77 | 85 |