

## Supporting Information for

### Reactions of Methane Monooxygenase Intermediate Q with Derivatized Methanes

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**Received April 17, 2002**

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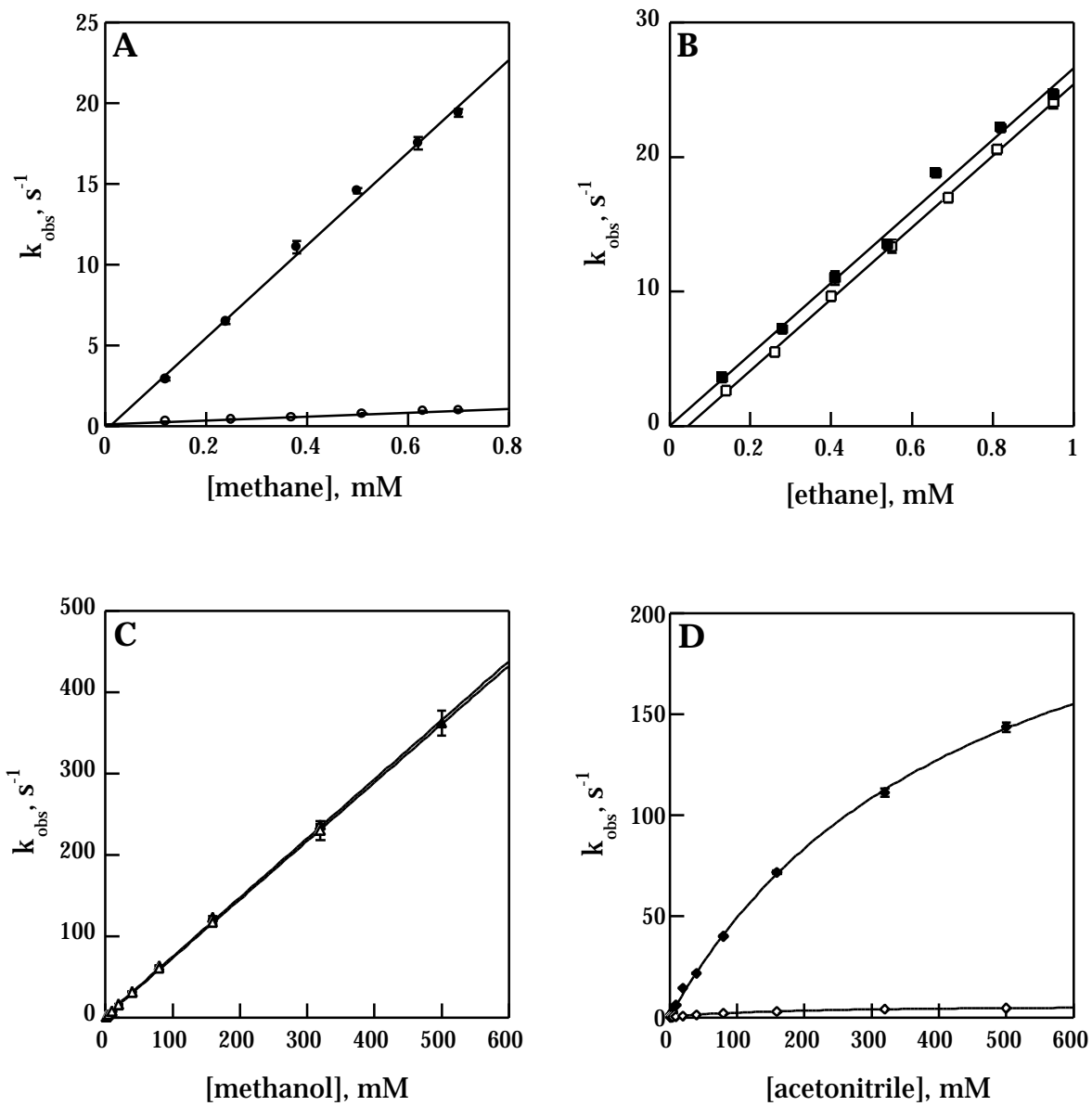
**Figure S1.** Plot of  $k_{\text{obs}}$  versus [substrate] for the following substrates: (A) methane, CH<sub>4</sub> (●), CD<sub>4</sub> (○), (B) ethane, C<sub>2</sub>H<sub>6</sub> (■), C<sub>2</sub>D<sub>6</sub> (□), (C) methanol, CH<sub>3</sub>OH (▲), CD<sub>3</sub>OH (△) and (D) acetonitrile, CH<sub>3</sub>CN (◆), CD<sub>3</sub>CN (◇).

**Figure S2.** Eyring plots for the decay of Q in the presence of substrates. Substrates tested were CH<sub>4</sub> (●), CH<sub>3</sub>CN (■), CD<sub>3</sub>CN (□), CH<sub>3</sub>OH (▲), CD<sub>3</sub>OH (△), CH<sub>3</sub>NO<sub>2</sub> (◆), CD<sub>3</sub>NO<sub>2</sub> (◇) and C<sub>2</sub>H<sub>6</sub> (×).

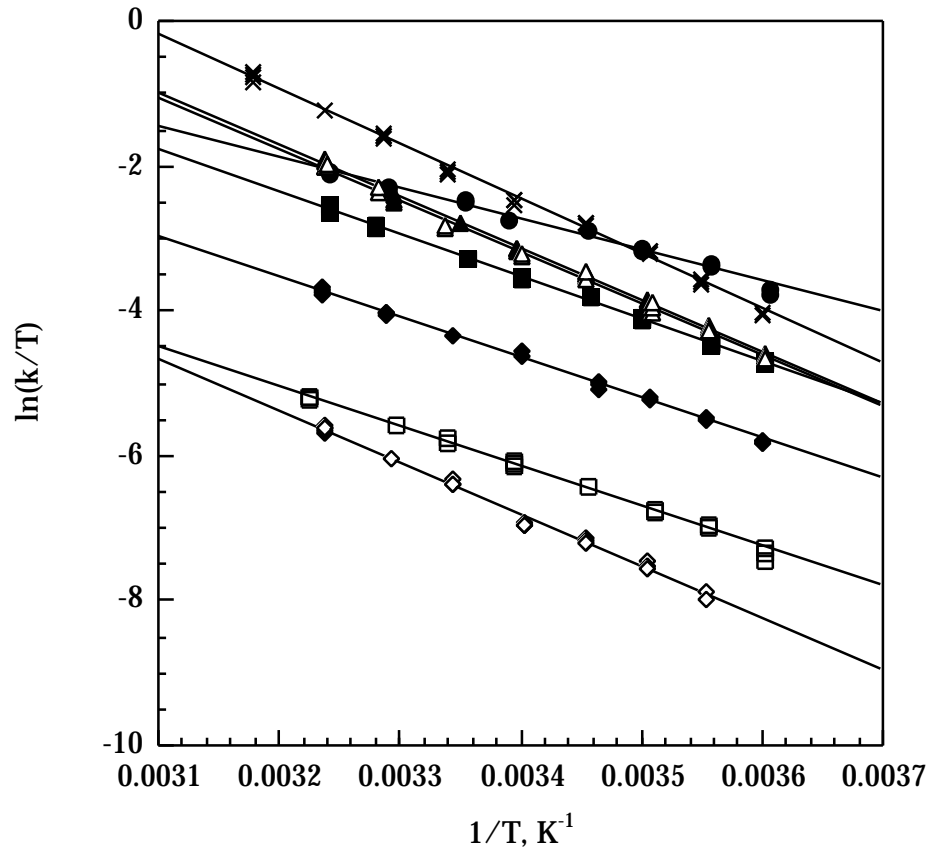
**Table S1.** Activation Parameters for the Decay of Q in the Presence of Substrates

| Substrates   | H <sup>‡</sup> , kcal/mol | S <sup>‡</sup> , cal/mol·K |
|--|---------------------------|----------------------------|
| CH <sub>4</sub> – 0.7 mM                               | 8.5 ± 0.3                 | -24 ± 1                    |
| C <sub>2</sub> H <sub>6</sub> – 0.95 mM                | 15.1 ± 0.2                | -0.9 ± 0.5                 |
| C <sub>2</sub> D <sub>6</sub> – 0.95 mM                | 13.3 ± 0.1                | -7.3 ± 0.5                 |
| CH <sub>3</sub> CN – 15.3 mM <sup>a</sup>              | 11.7 ± 0.1                | -14.5 ± 0.4                |
| CD <sub>3</sub> CN – 15.3 mM <sup>a</sup>              | 11.1 ± 0.2                | -21.8 ± 0.6                |
| CH <sub>3</sub> NO <sub>2</sub> – 20.0 mM <sup>a</sup> | 11.2 ± 0.1                | -18.5 ± 0.5                |
| CD <sub>3</sub> NO <sub>2</sub> – 20.0 mM <sup>a</sup> | 14.3 ± 0.2                | -12.2 ± 0.8                |
| CH <sub>3</sub> OH – 15.1 mM                           | 14.3 ± 0.2                | -4.8 ± 0.6                 |
| CD <sub>3</sub> OH – 15.3 mM                           | 14.1 ± 0.2                | -5.6 ± 0.7                 |

<sup>a</sup>Reactions with these substrates exhibit saturation kinetics.



Ambundo, Friesner and Lippard, Figure S1.



Ambundo, Friesner and Lippard, Figure S2.