# Reply to Comment on "Branching Ratios in Activated Systems"

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In our paper,[1] we used quantum RRK theory to demonstrate that the logarithmic relationship (1) is likely reasonable, but not strictly true, for a series of chemically activated reactions. Klots[2] notes that the same conclusions can be obtained from finite heat bath theory (FHBT). Klots's derivation is elegant and concise and provides the same cautions for the use of (1) that arose from our study.

$$\Delta \ln(k_1/k_2) \propto \Delta(\Delta E_1 - \Delta E_2) \tag{1}$$

Both treatments are based on unimolecular rate theory, and both contain assumptions. The RRKM calculations performed in our work, however, demonstrated that these assumptions are unlikely to influence the general form of the energy dependence for systems of reasonable size. For a single potential energy surface, (1) is generally valid, and the basis of its validity can be seen in either the simple combinatorics of the quantum RRK derivation or the FHBT derivation. For a series of reactions, changes in either the relative entropies of the competing pathways or the heat capacity (related to vibrational degrees of freedom or number of oscillators in the RRK formalism) of the system will influence the branching ratio. Experimentally, these considerations are generally met by studying a homologous series of reactions. The theoretical treatments present a valuable mechanism for understanding the limits of the relationship.

## References and Notes

(1) Craig, S. L.; Zhong, M.; Choo, B.; Brauman, J. I. *J. Phys. Chem. A* **1997**, *101*, 19−24.

(2) Klots, C. E. *J. Phys. Chem. A* **1997**, *101*, 5378.

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