# Elementary Steps in Metal-mediated Oxygenation of Hydrocarbons: An Intersection of Experiment and Theory

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Gas-phase experiments are ideally suited to probe, in the absence of obscuring effects, the role of electronic structures of "bare" transition-metal oxides in their reactions with hydrocarbons.

To this end, mass-selected, electronic ground states of cationic metal oxides are prepared and, under single-collision conditions, reacted with various substrates. These molecular beam experiments permit to determine directly at a molecular level

- reaction rates
- kinetic isotope effects
- bond dissociation energies
- branching ratios.

Based on these experimental findings and in combination with computational studies, the potential energy surfaces for the seemingly simple process (1) are constructed

$$MO^+ + RH \rightarrow M^+ + ROH \qquad (1)$$

It will be shown that, for some transition-metal oxides (e.g. $FeO^+$) the reactions cannot be described in terms of a single-potential energy surface. Rather, two different spin states play a decisive role in the oxygen atom transfer process. Consequences of these findings for the interpretation of P-450 mediated hydrocarbon oxygenation will be discussed [1,2,3].

[1 ] D. Schröder, S. Shaik, H. Schwarz, Acc. *Chem. Res.* **2000**, *33,* 139 - 145: "Two-State Reactivity as a New Concept in Organometallic Chemistry".

[2] D. Schröder, H. Schwarz, *Essays in Contemporary Chemistry: From Molecular Structure towards Biology* (Eds. G. Quinkert, M. V. Kisakürek), Wiley *2001,* 131 - 156: "Reactivity Concepts for Oxidation Catalysis: Spin and Stoichiometry Problems in Dioxygen Activation".

[3] S. Shaik, S. P. de Visser, F. Ogliano, H. Schwarz, D. Schröder, Curr. Opin. *Biology,* in press: "Two-State Reactivity (TSR) Mechanisms of Hydroxylation and Epoxidation by Cytochrome P-450 Revealed by Theory".