Mechanistic and Computational Studies of Ferroin, Organic Acids, and Bromine Oxides:

Elucidating the Complex Electrochemical Dance in an Oscillating Reaction

Cory T. Camasta

Rainer Glaser, Thesis Supervisor

ABSTRACT

Includes computationally derived data and literature reviews relating to autocatalytic or oscillating chemical reactions, specifically a ferroin-catalyzed Belousov-Zhabotinsky reaction. Mechanisms that cause the reaction to cycle from reactants to products and back are examined in terms of their thermodynamic viability and velocity. Physical mechanisms of electron transfer in ferroin and related transition-metal complexes are also examined, including references to similar phenomena in nature. Results indicate that geometrically strained transition metal complexes generally prefer to exist in low-spin states, while flexible and/or asymmetric complexes tend to favor more unpaired electrons. The study concludes that bromine oxides with stoichiometric formulas Br_2O, Br_2O_3, Br_2O_4 (BrO_2), and Br_2O_5 likely play more significant roles in the reaction dynamics than previously postulated. Since halogen oxides are also known to cause ozone (O_3) decomposition in the troposphere and stratosphere, this natural cycle is also discussed. Specific reactions are proposed with kinetic first-order rate constants that may improve the experimental agreement of future models.