Reply to "Mechanism of the Oscillatory Bromate Oxidation of Sulfite and Ferrocyanide in a CSTR"

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Rábai et al.[1] (RKH) have suggested that the dynamical behavior of the bromite−sulfite−ferrocyanide (BSF) system is better described by a mechanism that includes the component reaction of bromate and sulfur(IV)[2] than by the mechanism proposed by Edblom et al.[3] (ELOKE), which focuses more on the reactions of various bromine species. RKH contend that their mechanism fits the data as well as the ELOKE mechanism and is more consistent with independent kinetic studies.[4,5] We have reexamined the proposed mechanisms for the BSF system and present our findings here.

RKH present relatively limited data. We have utilized numerical simulation and bifurcation methods to test their mechanism and to compare it to the ELOKE mechanism under a wide range of conditions corresponding to those studied experimentally. We find that: (1) The RKH mechanism does an excellent job of simulating the batch bromate−sulfite reaction but performs less well than the ELOKE mechanism in simulating the batch behavior of the full BSF system, where simulations give a sharp rise in pH after the BrO_3^-−HSO_3^- reaction terminates, a phenomenon not seen in either the experiments or the ELOKE simulations. (2) Simulations of the BSF system in a flow reactor give qualitative agreement with the experimental oscillations using either mechanism, but the RKH oscillations have a period that is shorter and an amplitude that is larger than found experimentally and with the ELOKE mechanism. (3) Both mechanisms satisfactorily simulate the bistability between the high- and low-pH states. (4) Both mechanisms give good qualitative agreement with the phase diagram of the BSF system in the input sulfite−flow rate parametric plane.

We conclude that, despite minor quantitative differences, both mechanisms give satisfactory agreement with experiment. This observation is not surprising since steps B2−B6 in the ELOKE mechanism, which are not included in the RKH mechanism, are fast reactions that, together with the rate-determining step B1, yield the key overall reaction 1 in the RKH scheme. More generally, Luo and Epstein[6] derived from the ELOKE mechanism a five-step, four-variable model for pH oscillators that includes a fast protonation equilibrium, autocatalytic formation of H^+, and consumption of protons. The RKH mechanism may be viewed as a specific case of the general model with the Williamson−King[2] mechanism for the BrO_3^-−S(IV) reaction and the two sulfite protonation equilibria providing the autocatalytic pathway.

We agree that the RKH mechanism does an adequate job of simulating the available experimental data for the BSF system while dealing more satisfactorily with additional kinetic measurements[4,5] than does the ELOKE model. Our calculations reveal that the RKH model is extremely sensitive to the values of rate constant k_1 and k_2; similarly, the ELOKE model is sensitive to k_1. Both models fail to give even qualitative agreement with experiment when the rate constants found by Williamson and King[2] are used. It may be beneficial to reexamine the rate constants and the rate laws in the BrO_3^-−HSO_3^-/H_2SO_3 reactions under the conditions of pH oscillation in the BSF system and to apply the results in model simulations.

References and Notes

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