2,3-dimethyl-2-butene, 563-79-1; 1-hexene, 592-41-6; cyclohexene epoxide, 286-20-4; 2,3-dimethyl-2-butene epoxide, 5076-20-0; 1-hexene epoxide, 1436-34-6; *trans*-stilbene epoxide, 1439-07-2; 2-cyclohexen-1-ol, 822-67-3; 2-cyclohexen-1-one, 930-68-7; PhCHO, 100-52-7; [Cu(CH_3-$CN)_4](NO_3)$, 14057-91-1.

Washout Effects in Pumped Tank Reactors

N. Ganapathisubramanian and Kenneth Showalter*

Department of Chemistry, West Virginia University
Morgantown, West Virginia 26506-6045

Received September 30, 1983

Studies of multiple steady states in continuous-flow stirred tank reactors (CSTR) typically depend on the systematic variation of reactor residence time or some other system constraint such as reactant concentration. The concentration of an intermediate species is usually monitored as a function of time at a particular residence time until a steady state is established; the flow rate is then changed to give a new residence time and the next steady state concentration is determined. At short reactor residence times, the reaction mixture composition approaches the composition of the combined reactant streams; at long residence times, the composition approaches that corresponding to a batch reaction at thermodynamic equilibrium. For most chemical reactions, the steady-state concentration of a particular species is a continuous, smooth function of residence time between the extremes of zero and infinity. However, in a number of autocatalytic reactions,[1-8] the branch of steady states asymptotic to the reactant stream composition and the branch asymptotic to the equilibrium composition do not connect in a continuous fashion, but instead overlap one another. Thus, when a system constraint such as residence time is varied, a hysteresis effect is observed as the system moves from one branch of steady states to the other and back again. The system may exist in either of two steady states in the overlap region, i.e., the system is bistable.

The familiar pattern of steady-state multiplicity is dramatically altered when a minor modification is made in pumping the CSTR. A simple model system recently proposed by Gray and Scott,[9] which combines third-order autocatalysis with a first-order decay of the autocatalytic species, exhibits a second hysteresis region and may even give rise to an isolated branch of steady states. We recognized that a first-order decay of all species in a tank reactor can be provided by supplying a constant flux of solvent to the CSTR in addition to the flux of reagents.[10] In addition, the bistable iodate–arsenous acid reaction exhibits third-order autocatalysis[11] and, therefore, is an ideal chemical system for testing the model predictions. In this communication we report the first experimental characterization of a mushroom (two connected hysteresis regions) and an isola (an isolated branch of steady states) exhibited by a chemical system in an isothermal CSTR.

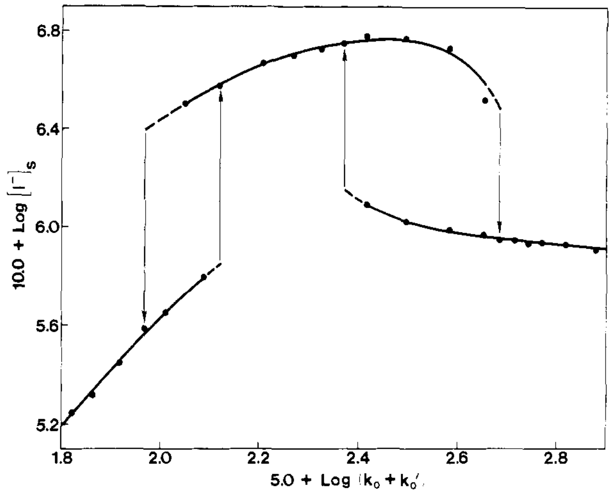

Figure 1. Steady-state iodide concentration (M) as a function of reciprocal residence time (s^{-1}). Concentrations in combined reactant streams: $[KIO_3]_0 = 1.01 \times 10^{-3}$ M; $[KI]_0 = 8.40 \times 10^{-5}$ M; $[H_3AsO_3]_0 = 4.98 \times 10^{-3}$ M. Solvent stream, $k_0' = 4.91 \times 10^{-4}$ s^{-1}; temperature, 25.0 ± 0.1 °C. Buffer in reactant streams and in solvent stream prepared with $NaHSO_4$ and Na_2SO_4 to yield a reaction mixture of pH 2.23.

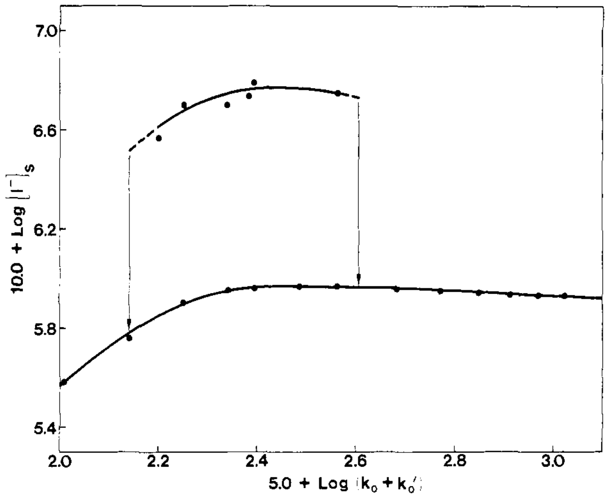

Figure 2. Same concentrations and conditions as in Figure 1 except $k_0' = 6.20 \times 10^{-4}$ s^{-1} for solvent stream.

Our investigation utilized a bistable iodate–arsenous acid system with arsenous acid in stoichiometric excess. An additional constant flow of solvent, consisting of a buffer solution identical with that in the reactant stream, was introduced to the CSTR. Figure 1 shows steady-state iodide concentrations as a function of reciprocal residence time (volume flow rate/tank volume). Here, the reciprocal residence time is given by the sum ($k_0 + k_0'$), where k_0 corresponds to the reactant stream and k_0' corresponds to the constant flow of buffer solution. We see that as reciprocal residence time is increased, a discontinuous increase in iodide concentration is found at a reciprocal residence time of 1.32×10^{-3} s^{-1}, and a discontinuous decrease occurs at 4.84×10^{-3} s^{-1}. As reciprocal residence time is decreased, the iodide concentration again increases at 2.34×10^{-3} s^{-1}, and it again decreases at 9.44×10^{-4} s^{-1}. The double hysteresis gives rise to a mushroom-shaped curve.

An important difference between the experiment reported here and earlier studies of bistability can be seen in Figure 1. For nonzero values of k_0', corresponding to a finite flux of additional solvent, the concentrations of all species approach zero as the value of reciprocal residence time approaches k_0'. This "washout" is evident in Figure 1 at low reciprocal residence times. As reciprocal residence time is increased to the first hysteresis limit, iodide

---

(1) Geiseler, W.; Föllner, H. H. *Biophys. Chem.* **1977**, *6*, 107–115.

(2) Papsin, G. A.; Hanna, A.; Showalter, K. *J. Phys. Chem.* **1981**, *85*, 2575–2582.

(3) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* **1981**, *103*, 6121–6127.

(4) Reckley, J. S.; Showalter, K. *J. Am. Chem. Soc.* **1981**, *103*, 7012–7013.

(5) Dateo, C. E.; Orbān, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 504–509.

(6) Orbān, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5911–5918.

(7) Orbān, M.; Epstein, I. R. *J. Am. Chem. Soc.* **1982**, *104*, 5918–5922.

(8) Orbān, M.; Epstein, I. R. *J. Phys. Chem.* **1983**, *87*, 3212–3219.

(9) (a) Gray, P.; Scott, S. K. *Chem. Eng. Sci.* **1983**, *38*, 29–43; (b) *J. Phys. Chem.* **1983**, *87*, 1835–1838.

(10) A first-order decay of all species gives rise to the same patterns of multiple steady states as those predicted by the model system of Gray and Scott;[9] however, the systems differ in their stability properties.[13]

(11) Ganapathisubramanian, N.; Showalter, K. *J. Phys. Chem.* **1983**, *87*, 1098–1099, 4014.

0002-7863/84/1506-0816$01.50/0

concentration increases to approximately its concentration in the combined reactant streams, which is also its concentration in the flow branch at high reciprocal residence times.

Figure 2 shows the appearance of an isola when the flow of buffer is increased. With increased solvent flow, the mushroom is squeezed off at the base leaving an isolated branch of steady states. Now as the reciprocal residence time is increased from the minimum possible value k_0', the system moves along a continuous branch of steady states. At appropriate reciprocal residence times, microliter injections of KI reagent result in perturbation-induced transitions from the continuous branch to the isola branch. Steady-state iodide concentrations and extinction points of the isola branch can then be determined by variation of reciprocal residence time. A slight maximum in steady-state iodide concentration is displayed in the continuous branch below the isola. The conversion of iodate to iodide at this maximum is less than 1.0%; however, in the isola branch at the same reciprocal residence time (3.05×10^{-3} s^{-1}), the conversion is over 41.0%.[12]

The patterns of multiple steady states reported here have potential ramifications for commercial tank reactor processing. Thus, the conversion of reactants to products in the isola branch is many times greater than that in steady states ordinarily accessible by variation of system constraints. A simple model of the iodate–arsenous acid reaction[11] provides a near quantitative description of the patterns of steady states in this system. A detailed study of washout effects in the iodate–arsenous acid system will appear in another paper.[13]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8311360).

Registry No. Iodate, 15454-31-6; arsenous acid, 13464-58-9.

---

(12) Here, conversion is defined simply as $([\mathrm{I}^-] - [\mathrm{I}^-]_0)/[\mathrm{IO}_3^-]_0$. An alternate definition of conversion which accounts for washout of reactants and products is $((k_0 + k_0')[\mathrm{I}^-] - k_0[\mathrm{I}^-]_0)/k_0[\mathrm{IO}_3^-]_0$.[13]

(13) Ganapathisubramanian, N.; Showalter, K. *J. Chem. Phys.*, in press.

Powder ENDOR Analysis of the *p*-Benzosemiquinone Anion Radical

Pádraig J. O'Malley and Gerald T. Babcock*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824-1322

Received July 5, 1983

EPR and ENDOR spectroscopies have been used extensively in the study of biological free radical systems.[1,2] Quinones, which perform various functions in biological systems, have represented an intense area of study for many years.[3] EPR analysis of the free radical signals arising from these quinones suffers, however, from the immobilized character and resulting lack of spectral resolution in the signals observed.[4,5] The investigator is therefore usually confined to spectral quantities such as line width, line-shape characteristics, and average g value determinations. Important parameters, such as the nuclear hyperfine interaction, are usually lost in the inhomogeneously broadened spectrum. The infeasibility of single-crystal studies, particularly in biological membrane systems, therefore puts severe limitations on the amount of information available from such studies.

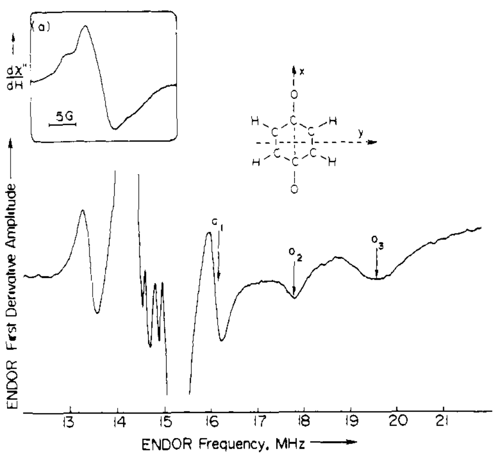

Figure 1. ENDOR spectrum of the *p*-benzosemiquinone anion radical at 123 K: mW powder, 6.3 mW; rf power, 150 W at 12 MHz; FM modulation, ±150 kHz; time constant, 2 s; sweep time, 500 s; average of 17 scans. For explanation of spectral region 14–16 MHz, see ref 20. Inset a: EPR spectrum: mW power, 200 μW; modulation amplitude, 2.0 G; time constant, 50 ms; sweep time, 100 s. Inset b: g tensor principal axes as described by Hales.[16]

Table I. Principal Values of Hyperfine Tensor for the α-CH Proton of *p*-Benzosemiquinone Anion Radical Compared with Theoretical Dipole–Dipole Interaction Values for an Isolated C–H Fragment[a,17,18]

	$T_\perp$	T_{CH}	T_π	ρ^c	angle of hf axis and C–H bond direction
theory[b]	−13.6	15.4	−1.7	1.0	0°
	−1.1	1.2	−0.1	0.08[d]	0°
experimental	−1.2	1.3	0.0	0.08[d]	

[a] All values are in gauss (G). $T_{\mathrm{i}} = a_{\mathrm{i}} + 2.2$ (isotropic value). All a_{i} values are taken as negative. [b] From ref 17 and 18. [c] Spin density. [d] Determined by using the relationship a_{i}(isotropic) = $Q\rho_{\mathrm{i}}$ using $Q^{\mathrm{CH}} = -27$ G.[21]

Although the ENDOR technique has been used to considerable advantage in the investigation of other biological radicals (e.g., the chlorophylls[6-8]), such studies have been principally concerned with β-proton interactions. For the more highly anisotropic α protons, a severe broadening of the ENDOR band over a wide spectral range usually occurs. A buildup of intensity at the principal hyperfine tensor values is expected for α protons.[9] Unfortunately, the quality of the spectra so far obtained have precluded such an analysis.[10,11]

We report here that as the result of increased sensitivity of detection, we have been successful in obtaining the principal hyperfine tensor values of the *p*-benzoquinone anion radical from its powder ENDOR spectrum (Figure 1). The formation of fixed hydrogen bonds between the quinone carbonyls and the ethanol hydroxyl group, originally proposed by Hales[15,16] from EPR line-width broadening and anisotropic saturation effects, is confirmed by the presence of an intense band in the ENDOR spec-

---

(1) Swartz, H. M.; Bolton, J. R.; Borg, D. C. "Biological Applications of Spin Resonance; Wiley: New York, 1972.

(2) Kevan, L.; Kispert, L. C. "Electron Spin Double Resonance Spectroscopy"; Wiley: New York, 1976; pp 388–414.

(3) Das, M. R.; Connor, H. D.; Leniart, D. B.; Freed, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 2258.

(4) Hales, B. J.; Case, E. L. Biochim. *Biophys. Acta* **1981**, *637*, 291.

(5) Klimov, V. V.; Dolan, E.; Shaw, E. R. Ke, B. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*.

(6) Feher, G.; Hoff, A. J.; Isaacson, R. A.; Ackerson, L. C. *Ann. N.Y. Acad. Sci.* **1975**, *244*, 239.

(7) Lubitz, W. "Proceedings of the International Conference on Electron Spin Resonance of Radicals in Organic and Bio-Organic Systems"; Nottingham University Press: Nottingham, England, 1982.

(8) O'Malley, P. J.; Babcock, G. T. *Proc. Natl. Acad. Sci. U.S.A.*, in press.

(9) Reference 2, p 234.

(10) Hyde, J. S.; Rist, G. H.; Erickson, L. E. G. *J. Phys. Chem.* **1968**, *72*, 4269.

(11) For radicals in which a large g factor or hyperfine (a) anisotropy does exist orientation selection can be carried out by monitoring the so-called turning points of the EPR spectrum while sweeping through the desired RF frequency range.[12,13] For simple carbon-based organic radicals, which exhibit relatively low anisotropy in their g and a values, species selection such as the above is not possible at X-band frequencies.

(12) Allendoerfer, R. D. *Chem. Phys. Lett.* **1972**, *17*, 172.

(13) Schweiger, A.; Rudin, M.; Gunthard, Hs. H. *Chem. Phys. Lett.* **1983**, *95*, 285.

(14) Hyde, J. S. *J. Chem. Phys.* **1965**, *43*, 1806.

(15) Hales, B. J. *J. Chem. Phys.* **1976**, *65*, 3767.

(16) Hales, B. J. *J. Am. Chem. Soc.* **1975**, *97*, 5993.

0002-7863/84/1506-0817$01.50/0