The Effect of Mixing-Induced Noise on Second Order Reactions in a CSTR

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The effects of inhomogeneity of a reacting system on the chemical rate and dynamics have received different attention in the chemical engineering and chemical kinetics communities. While the hydrodynamics of mixing and its effects on simple reactions are well-developed subjects of the chemical engineering curricculum,[2] chemical kineticists usually treat rapidly reacting systems as if they were homogeneous[3] and little is known quantitatively[4] about the dependence of rate and conversion on the mixing-induced noise that arises from the system's inhomogeneity—except for diffusion-limited reactions.[5] In stirred flow reactors, e.g., the continuous flow stirred tank reactor (CSTR), there exists a continuum of inhomogeneity or segregation, and the kinetics depends intricately on the hydrodynamic state through the design of reactor and stirrer and through the stirring rate and mixing mode, i.e., the use of a single, premixed (PM) or of separate, nonpremixed (NPM) reactant feedstreams.[2] Recent studies in different fields of science, as far afield as stratospheric chemistry and oceanography, have shown that noise can play an enhancing role in dynamical systems.[6]

The aim of this Communication is to show, by experiment and simulation, that progress may be made by taking into account the noise generated by the mixing process and seen by a fixed detector and that it is possible to account quantitatively for the inhomogeneous kinetics in a CSTR. For the experiment we use the second order reaction[7]

$$2Fe^{2+} + NO_2^- + 2H^+ \rightarrow 2Fe^{3+} + NO + H_2O \qquad (1)$$

Its rate law is $dx/dt = -kx^2 + k_o(x_o - x)$ when the inflow concentrations $x_0 = [Fe^{2+}]_0 = [NO_2^-]_0$ are equal and where $x = [Fe^{2+}]$. k_0 is the inverse residence time.

Imperfect mixing is taken into account by assuming perfect macromixing and by describing the micromixing process in terms of the stochastic steady state of the reactor,[8] i.e., by the first (x_s) and the second (σ^2) moments of the fluctuating concentration. In the well-stirred limit $\sigma^2 \rightarrow 0$ one usually considers only the deterministic state (x_d). Recently we showed theoretically[8] that there exists a linear correlation between the shift $\Delta = x_s - x_d$ of the stochastic steady state from its deterministic limit and the variance σ^2 of the mixing-induced noise

$$\Delta = \alpha(k,k_o,x_o)\sigma^2 \qquad (2)$$

where the proportionality constant α is determined only by the rate law and the deterministic rate parameters for a given mixing mode.[9]

The experiments were conducted in a cylindrical CSTR[8] at $T = 22$ °C, using a two-blade propeller stirrer in the range $S = 0-1500$ rpm. Reactants were stored in two solutions: (A) 0.0071 M KNO_2 (B) 0.0071 M $FeSO_4$; 2 M H_2SO_4 which were pumped into the reactor either in two NPM streams entering at the bottom (B) and at the top (A) of the reactor or combined just prior to entering into a single PM stream. The state of the system was monitored by a Pt electrode (0.1 mm Pt wire fused in glass, 0.2 mm long) relative to a $Hg/HgSO_4$ reference electrode. Control experiments showed that the observed fluctuations of the signal arose primarily from reactive mixing.[17]

Figure 1 (parts a and b) show the time average (E_{Pt}) and the variance (σ^2) of the measured Pt-electrode potential as functions of the stirring rate (S) for PM (closed circles) and NPM (open circles) feedstream configurations. It is evident that increasing the inhomogeneity by decreasing stirring from its maximal value ($S = 1500$ rpm) to nonstirred conditions ($S = 0$ rpm) decreases the potential (and increases $[Fe^{2+}]$, hence decreases the reaction rate) in the NPM mode (Figure 1a). In the PM mode the opposite is true, and decreased stirring increases the reaction rate. Decreased stirring also increases the noise (σ^2) in both mixing modes as expected (Figure 1b), and the variance is always higher in the NPM mode than in the PM mode. Despite the different dependence of the average potential (concentration) and its

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(9) For second-order reactions in a CSTR with PM feedsreems $\alpha = -k/(4kx_d + 2k_0)$. This expression is obtained using results of ref 8 and a technique developed in (a) Evangelista, J. J.; Katz, S.; Shinnar, R. *A.I.Ch.E.J.* **1969**, *15*, 843−853. (b) Hannon, L.; Horsthemke, W. *J. Chem. Phys.* **1987**, *86*, 140−143. With this equation, the deterministic, well stirred steady state may be obtained in nondimensional form from $(x_d/x_0) = (x_s/x_0) = [4(x/x_0) + 2(k_0/kx_0)]^{-1}(\sigma/x_0)^2$.
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(11) Figure 1 gives the average potential and its variance as functions of S and the linear scaling between the shift of the average potential and its variance. To obtain the average Fe^{2+} concentration and its variance from the raw data using a calibration plot between E_{Pt} and $[Fe^{3+}]/[Fe^{2+}]$ is possible for the PM mode only because the conservation $[Fe^{3+}] + [Fe^{2+}] = [Fe^{2+}]_0$ is valid in every subvolume of the reactor for the PM mode but not for the NPM mode. Thus the linear scaling (2) was rigorously confirmed for PM and approximately for NPM, based on simplifying assumptions. Nevertheless we present in Figure 1c the scaling of electrode potential and its variance to emphasize that the scaling (2) applies also to experimental raw data. This different representation of experimental results and of simulations accounts for the opposite slopes in Figures 1and 2.
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(17) In control experiments without reaction, using a single feedstream (B) that contained $FeSO_4 + H_2SO_4$, the noise amplitude was 4−5x smaller than in the presence of reaction. Likewise, it was ascertained that in the absence of the propeller-stirrer, electromagnetic radiation from the stirring-motor alone contributed negigibly to the observed fluctuations of the signal.

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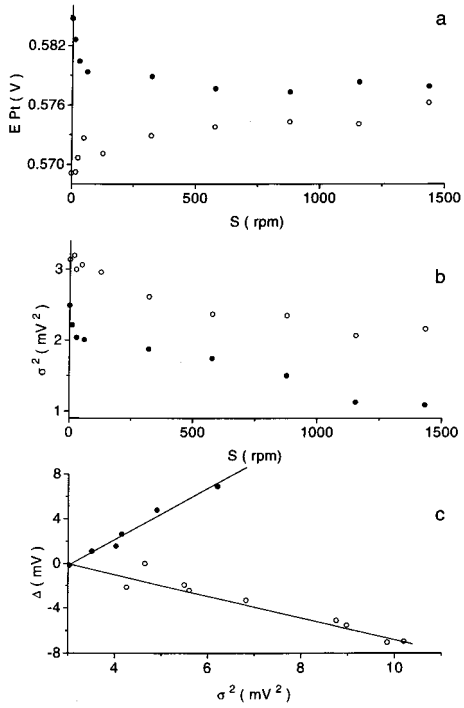

Figure 1. Dependence of the system response on stirring rate: (a) time average of the Pt-electrode signal and (b) its variance. Panel (c) gives the linear relationship between the shift $\Delta = E_{Pt}(S) - E_{Pt}(1500)$ and the variance σ^2. Open circles − NPM mode, closed circles − PM mode.

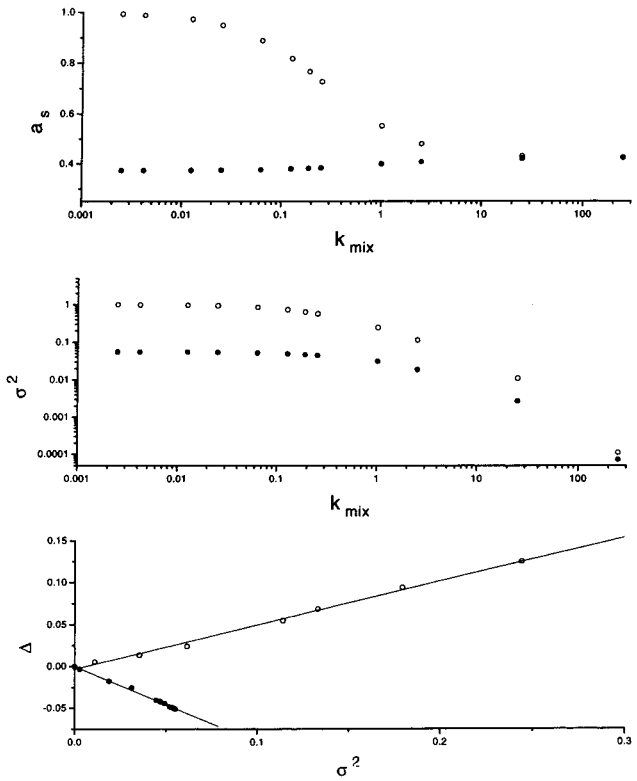

Figure 2. Dependence of (a) the average reactant concentration (a_s) and (b) its variance on the mixing rate, obtained by simulations for the bimolecular reaction $A + B$ in a CSTR ($[A]_0 = [B]_0 = 1$; $k = 0.4$, $k_0 = 0.125$). Panel (c) illustrates the linear relation between the shift $\Delta = a_s - a_d$ and the variance σ^2 for both PM and NPM modes. Symbols as in Figure 1.

variance, the generic relationship (2) between these quantities is fulfilled. Figure 1c confirms the linear scaling (2) between the shift Δ of the stochastic steady state from its deterministic limit and the mixing-induced noise σ^2 for both mixing modes.[11] The linear regression coefficient is $R > 0.987$ for both data sets.

To confirm that the linear scaling relation $\Delta(\sigma^2)$ is generic for both mixing modes, we performed simulations of the bimolecular reaction $A + B$ in a CSTR using the coalescence-redispersion micromixing model[10] which describes the interaction between mixing, feeding, and chemical relaxation. It treats the CSTR as a large number of identical cells which evolve like batch reactors. Flow is represented by randomly choosing cell(s) at fixed intervals and replacing them by fresh reactants, PM or NPM as the case may be. Mixing is represented by averaging the concentrations of randomly chosen pairs with rate $k_m \sim S$. Figure 2a,b gives the average concentration a_s and its variance σ^2 of the reactant A as functions of mixing rate. These results are in good agreement with experiments.[11] The slope α of the dependence of Δ on σ^2 coincides with that predicted by theory for PM feedstreams.[9] The analysis of experimental results for different concentrations, flow, and stirring rates and the corresponding simulations show that the linear scaling law (2) is valid for both feedstream configurations and for any parameter values.

The experiments and simulations reported here confirm that stirring in PM and NPM feeding modes has opposite effects.[2] "Stream mixing" of separate NPM feedstreams brings reactants into contact and thus enhances the reaction rate, while "age or back mixing" of PM feeds dilutes the inflow in which the reactant concentration and hence the reaction rate are maximal, and therefore decreases the overall rate. Most importantly in the present context, the results show that in both mixing modes the reacting systems respond linearly to the intensity σ^2 of mixing-induced noise. This scaling does not depend on the particular source of imperfect mixing and on the experimental setup. If, for some reason, one cannot eliminate mixing-induced noise from the signal, then it is possible to account for its presence by using the linear scaling law (2) by extrapolating to the infinite stirring limit $\sigma^2 \rightarrow 0$. This may be useful in stopped-flow studies of chemical kinetics,[12] in ultrafast dynamics,[13] biological chemistry,[14] chemical engineering,[2] atmospheric and stratospheric chemistry,[6] i.e., in studies where mixing-induced noise is naturally present and cannot be eliminated.

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