AN EPR STOPPED-FLOW KINETIC STUDY OF Mn(II) SORPTION ON MnO_2

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Metal ions have a profound influence on the environment, acting as both a potential environmental hazard, and, when incorporated into a solid phase, as a retention sink for pollutants. Often kinetic pathways control the fate of metal ions rather than equilibrium factors. Furthermore, reaction mechanisms can be ascertained when one measures chemical kinetics devoid of transport phenomena. Thus, important reaction rates and mechanisms can be obtained through a chemical kinetic investigation.

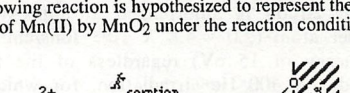
Many soil and environmental chemical processes are rapid, and thus have precluded the use of traditional batch or flow techniques for kinetic measurements.[1] Chemical relaxation techniques have been used to investigate rapid suspension reactions by monitoring a system parameter related to a species concentration (e.g., electrical conductivity) which is not adversely affected by the presence of colloidal material.[2-5] However, with many of these techniques the reaction must be fully reversible, reactant species are not directly measured, and rate constants are determined from linearized rate equations that often are dependent on equilibrium parameters. In this study, we demonstrate the utility of a stopped-flow kinetic technique monitored by electron paramagnetic resonance (EPR) spectroscopy for measuring rapid reactions in colloidal suspensions. The EPR-SF technique eliminates the conventional limitations of measuring colloidal reactions, allowing for direct measurement of a reactant species *in situ* on a millisecond time scale.

The binding of solution species to solid surfaces present in soil and water systems is a primary determinant in the behavior of many substances. Such processes can tie-up plant nutrients, remove hazardous contaminants, and modify mineral surfaces. The sorption/desorption of Mn(II) on Mn-oxides represents a means of removal for this metal ion, and may also alter the properties of the Mn-oxide, thus, influencing the oxidative ability of this oxide. Therefore, it was the intent of this study to determine the rates and mechanisms of Mn(II) sorption on δ-MnO_2.

The EPR-SF method entailed a two-port rapid injection of reactants, MnO_2 and Mn(II), into an EPR mixing cell. Measurements were limited by the mixing rate, allowing detection within 10 ms. Equal volumes from each syringe are injected into the mixing cell which gave initial reactant concentrations of 25 and 40 μM Mn(II) and 0.5 g L^{-1} MnO_2. The reactions were carried out at pH = 5.0 in 0.001M $NaNO_3$. The EPR signal was related to [Mn(II)] (here, brackets denote concentration units), and was linear over the concentration range of 5-500 μM. Further details of the EPR-SF method can be found elsewhere.[6]

At pH=5, the surface functional groups of δ-MnO_2 are in their fully deprotonated (oxo) state, and thus H^+ does not enter the reaction for the conditions invoked in this study. Furthermore, the reaction rate was not influenced by further increases in solution pH. Hence, the forward reaction should be dependent on solution Mn(II) and the surface site concentration of MnO_2. The reverse reaction would be dependent on the amount of Mn(II) complexed. By maintaining a large excess of sorbent over sorbate, and monitoring the reaction far from equilibrium where the reverse reaction rate should be minimal, the overall reaction should be pseudo first-order depending only on [Mn(II)]--permitting only the forward rate constant, $k_{sorption}$, to be measured. For the system parameters defined, the number of sorption sites would be at least two orders of magnitude greater than the number of Mn(II) ions present, even at the highest Mn(II) concentration.

The following reaction is hypothesized to represent the contributing species for the sorption of Mn(II) by MnO_2 under the reaction conditions employed in this study:



[1].

Reaction [1] is valid far from equilibrium where $k_{sorption} >> k_{desorption}$; thus, $k_{sorption}[Mn^{2+}] - k_{desorption}[Mn^{2+}] \approx k_{sorption}[Mn^{2+}]$. The rate dependence can be described as

$$R = -\frac{d[Mn^{2+}]}{dt} = = k\,[Mn^{2+}] \qquad [2]$$

where $k = k_{sorption}$[surface sites]. In order to deduce mechanistic information on the sorption of Mn(II) on δ-MnO_2 and to confirm the reaction order, two initial concentrations of Mn(II) were used, 40 and 25 μM. The rate constants obtained for the first-order reaction mechanism are -3.60 x 10^{-3} s^{-1} and -3.72 x 10^{-3} s^{-1} for 25 μM and 40 μM $[Mn^{2+}]_0$, respectively, with an averaged k = -3.66 x 10^{-3} ± 0.6 x 10^{-3} s^{-1}. The validation of reaction [1] as a first-order elementary reaction indicates that chemical kinetics were measured.

Mn(II) sorption on Mn-oxides has important environmental implications; knowledge of reaction rates and mechanisms of this process are necessary to

understand and predict the fate of these constituents. Here, the EPR-SF technique has shown great utility for such an investigation.

References

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