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KINETICS OF SOIL CHEMICAL PROCESSES: AN OVERVIEW

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Without question, one of the major current areas of interest in soil chemistry research is kinetics of soil chemical phenomena. This topic is relatively new to our subdiscipline, and most certainly has not been a leitmotiv like soil acidity, ion exchange, equilibrium modeling, ion activities, etc. If one peruses the literature, one finds that early studies by Way and others (see Sparks, 1989) on ion exchange concluded that reaction rates were instantaneous. This conclusion is partially correct but as often happens in sciences may have been accepted as totally correct by many investigators. These investigators would have concluded that they could not measure reaction rates on soils. This may explain why such a paucity of research on kinetic phenomena appeared over the period from the 1850's to the mid-1900's. Only during the last 30 years and particularly the past ten years, have studies appeared on a regular basis on various aspects of kinetics of soil chemical phenomena. Reviews and books have been recently published which discuss this very important area of research (Sparks, 1986, 1987, 1989, 1990a,b). A major international symposium was held last year at the Soil Science Society of America meeting on kinetics of physicochemical processes of soils (Sparks and Suarez, 1990) and of course, this very timely international symposium is addressing recent developments in the soil kinetics area.

In this paper, I should like to present a succinct overview of the topic with particular emphases on some important recent developments in the areas of kinetic methodology and data interpretation and to suggest future research needs. My remarks will emphasize research in our own laboratories, but it should be recognized that excellent studies are being conducted by a number of research groups in the world; some of those groups are represented in this symposium.

Critique of Rate Laws and Data Interpretation

As we know, soils and even soil components, are complex, heterogeneous materials. The application of kinetics to such systems is arduous, and we must be cognizant of this when rate studies are planned in the laboratory and when kinetic data are interpreted. Although one may wish to determine the chemical kinetics of a system, viz., the study of chemical reaction rates and of the molecular processes by which reactions occur where transport is not limiting, one is in fact usually determining a combination of chemical kinetics and kinetics events. Kinetics simply refers to time-dependent phenomena, e.g., film, particle, and surface diffusion, and chemical kinetics (Aharoni and Sparks, 1990).

The determination of chemical mechanistic rate laws for soils, which assume that only chemical kinetics processes are being studied and that transport-controlled kinetics that involve

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physical aspects of the soils are not operational, is extremely difficult. This is largely attributable to the complexity and heterogeneity of soils and soil constituents. Heterogeneity is usually enhanced due to different particle sizes, types of external and internal sites, and porosities. Another complicating factor in determining chemical mechanistic rate laws for heterogeneous systems is the often observed dependence of reaction rate on stirring and flow rates, and other forms of mixing.

Thus, in almost all cases, soil chemists are measuring apparent rate laws since mass transfer and transport are being studied. There are a number of transport phenomena that occur in soil kinetic studies. These include: transport in the soil solution, transport across a liquid film at the solid/liquid interface, transport in liquid filled macropores, diffusion of the sorbate at the surface of the solid, diffusion of sorbate occluded in micropores, and diffusion processes in the bulk of the solid (Aharoni and Sparks, 1990). Any one or more of these transport phenomena and/or chemical reaction could be rate-limiting. In most soil chemical reactions, transport phenomena are rate-limiting.

An eclectic group of simple kinetic equations including various ordered expressions, e.g., zero-, first-, second-, and empirical equations such as Elovich, power, and parabolic diffusion have been employed to describe reaction rates in soils. Several studies have shown (see Sparks, 1989) that a number of the above equations equally well describe the experimental data which indeed seems singular.

In fact, it is usually difficult to apply simple kinetic equations to soils since the reacting surfaces are heterogeneous and one usually cannot delineate transport effects from chemical kinetics. Nonetheless, researchers continue to apply such models to an array of soil chemical reactions and unfortunately, to elucidate mechanisms based solely on the "fit" of an equation to the experimental data. Aharoni and Sparks (1990) have recently commented on these points and have shown that a generalized empirical equation can be derived by closely examining the applicability of power, Elovich, and apparent first-order equations to experimental data. These equations are given below,

\[ q = kt^n \]  

where \( q \) is the quantity adsorbed at time \( t \), and \( k \) and \( n \) are constants.

\[ q = A + (1/b) \ln (t + t_0) \]  

Elovich

where \( A \), \( b \), and \( t_0 \) are constants

\[ q/q_s = 1 - \alpha \exp(-\beta t) \]  

Apparent First-Order

where \( q_s \) is the maximum quantity adsorbed and \( \alpha \) and \( \beta \) are constants.

Differentiating these equations and writing them as explicit functions of the reciprocal of the rate \( (Z) = (dq/dt)^{-1} \), one can show that the plot of \( Z \) vs. \( t \) for an experimental isotherm should be convex if Eq. [1] is operational, linear if Eq. [2] is applicable, and concave if [3] is appropriate. However, Aharoni and Sparks (1990) have shown that \( Z \) vs. \( t \) plots for soil chemical reactions are usually S-shaped; convex at small \( t \), concave at large \( t \), and linear at some intermediate \( t \) range. This finding suggests that the kinetics follow some abstruse function that can be approximated by the power equation at small \( t \), by the Elovich
equation at an intermediate t, and by an apparent first-order equation at large t. One often assumes S behavior even where one of these three empirical equations seems to apply over the entire reaction period. The fact that equations like power, Elovich, and apparent first-order are approximations to which the general Z equation reduces at certain limited ranges of adsorption indicates why no consistent theoretical derivation can be found for these equations. It also helps explain why there is no correlation between the applicability of any of these equations and the nature of the retention processes viz, dissimilar processes are fitted by the same equation and similar processes are fitted by different equations. One must then critically question the meaning of conformity of rate data to various empirical and different ordered equations.

Aharoni and Sparks (1990) explain the meaning of S-shaped Z (t) plots by showing that equations for diffusion in homogeneous and heterogeneous media lead to such plots. In the former medium, equations for diffusion yield S-shaped Z (t) plots in which the final and initial curved parts dominate. Equations for diffusion in a heterogeneous medium provide S-shaped Z (t) plots in which the intermediate linear part is dominant. They also allow for the calculation of diffusion parameters.

Advances in Kinetic Methodologies

Various types of batch and flow techniques have been used to study the kinetics of soil chemical phenomena and their advantages and disadvantages are thoroughly reviewed in an especially careful and thoughtful review by Amacher (1990). Regardless of the technique one uses, none of them is a panacea for kinetic analyses. Batch methods involve agitation of the sorptive and sorbent by stirring or shaking and separation of the two by centrifugation or rapid filtration. Flow techniques include continuous and stirred-flow (Sparks, 1989; Amacher, 1990). The stirred-flow method developed by Carski and Sparks (1985) and modified by Seyfried et al. (1989) is especially attractive for studying soil chemical reactions. Attributes of this method include: reaction rates are independent of the physical effects of porous media, the same apparatus can be used to measure both equilibrium and kinetic parameters, continuous (or incremental) measurements allow monitoring of reaction progress, experimental conditions such as flow rate and soil mass can be easily manipulated, and the technique is suitable over a wide range of textures and colloidal particle sizes. The sorbent is dispersed, dilution errors can be accounted for, desorbed species are constantly removed, and perfect mixing occurs (Seyfried et al., 1989). Recently, tests involving flow rate, concentration, and stopped-flow experiments have been presented and verified so that one can differentiate between instantaneous equilibrium, kinetic reactions that are concentration dependent, and kinetic reactions that are concentration independent (Bar-Tal et al., 1990; Eick et al., 1990).

In the author's opinion, the stirred-flow technique can be used very successfully to study soil chemical reaction rates that are slower than 0.6 minutes. However, there are many reactions in soils that occur on millisecond and microsecond time scales. These include some ion adsorption/desorption, ion exchange,
proton hydrolysis, and complexation reactions (Sparks and Zhang, 1990). For such reactions, the application of chemical relaxation techniques is appropriate and offers some exciting and important advantages.

Examples of transient chemical relaxation methods include pressure-jump, temperature-jump, concentration-jump and electric field pulse (Sparks, 1989; Sparks and Zhang, 1990). With chemical relaxation methods, the equilibrium of a reaction mixture is rapidly perturbed by some external factor such as pressure, temperature, or electric field strength. Rate information can then be obtained by following the approach to a new equilibrium by measuring the relaxation time. The perturbation is small and thus the final equilibrium state is close to the initial equilibrium. Because of this, all rate expressions are reduced to first-order equations regardless of reaction order or molecularity. Therefore, the rate equations are linearized, simplifying determination of complex reaction mechanisms. For more complete information on the theoretical and experimental aspects of chemical relaxation, the reader is urged to consult Sparks (1989) and Sparks and Zhang (1990).

Zhang and Sparks (1989, 1990) were the first soil chemists to apply relaxation techniques to soil chemical reactions. They used a pressure-jump relaxation method to elucidate mechanisms for molybdate (Zhang and Sparks, 1989) and sulfate (Zhang and Sparks, 1990) adsorption/desorption on goethite. In the former study, a double relaxation was obtained: a fast relaxation that corresponded to times up to \( \approx 0.04 \) seconds and a slow relaxation occurring over a time range of \( \approx 0.04-0.20 \) seconds. Based on kinetic and equilibrium data, a two-step reaction mechanism given below was postulated and verified for molybdate adsorption/desorption on goethite:

\[
\begin{align*}
\text{Step 1} & : \quad \text{SOH}_2^+ + \text{MoO}_4^{2-} & \rightleftharpoons & \quad \text{SOH}^- \quad \text{and} \quad \text{MoO}_4^{2-} \\
\text{Step 2} & : \quad \text{SMO}_4^- + \text{H}_2\text{O} & \rightleftharpoons & \quad \text{SOH}^- + \text{MoO}_4^{2-}
\end{align*}
\]

Step 1 involved an outer-sphere complexation reaction, whereas Step 2, which was found to be rate-limiting, involved inner-sphere complexation. Linearized rate equations relating reciprocal relaxation times to the forward and backward rate constants for Step 1 (\( k_1^{\text{int}} \) and \( k_1^{\text{int}} \), respectively) and Step 2 (\( k_2^{\text{int}} \) and \( k_2^{\text{int}} \), respectively) were developed, tested, and found valid. Accordingly, the forward and backward rate constants were calculated from the slopes and intercepts, respectively of the linear plots and found to be: \( k_1^{\text{int}} = 4019.2 \text{ mol}^{-1}\text{Ls}^{-1} \), \( k_1^{\text{int}} = 391.5 \text{ s}^{-1} \), \( k_2^{\text{int}} = 1.89 \text{ mol}^{-1}\text{Ls}^{-1} \), and \( k_2^{\text{int}} = 42.34 \text{ s}^{-1} \).

Not only can one use relaxation techniques to measure very rapid reactions, but it also appears that one is measuring mechanistic rate laws, viz., chemical kinetics is being measured. Evidence for this is shown in Table 1 for sulfate adsorption/desorption (Zhang and Sparks, 1990) on goethite.

<table>
<thead>
<tr>
<th>( k_1^{\text{int}} )</th>
<th>( k_1^{\text{int}} )</th>
<th>( \log K_{\text{kinetic}}^{\text{int}} )</th>
<th>( \log K_{\text{static}}^{\text{int}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{mol}^{-1}\text{Ls}^{-1} )</td>
<td>( \text{s}^{-1} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( 2.02 \times 10^8 )</td>
<td>0.144</td>
<td>9.14</td>
<td>9.60</td>
</tr>
</tbody>
</table>

Table 1. Intrinsic rate and equilibrium constants for \( \text{SO}_4 \) adsorption on goethite as determined from kinetic and measurements. Zhang and Sparks (1986b).
The consistency between equilibrium constants calculated from equilibrium \((K_{eq})\) and kinetic \((K_r/k_1)\) approaches \((K_{kin})\) is excellent for both systems. Such findings have also been observed for ion exchange reactions (Ikeda et al, 1981).

**Future Research Needs**

It is clear from this short review that while there have been several advances in the study area of kinetics of soil chemical processes, there is a great need for further investigations. Future research needs include: improved kinetic methodologies; more complete and careful data interpretation; use of spectroscopy with kinetic experiments to ascertain reaction mechanisms; use of relaxation techniques to measure rapid soil chemical reactions; effect of selectivity on rates of reactions; development of improved models that incorporate experimentally determined kinetic parameters; kinetics of ternary and quaternary exchange phenomena, more computer software packages for analyzing rate data; kinetic studies on pesticide and organic pollutant interactions with soils, and kinetics of reactions on humic substances. Obviously, our understanding of kinetics of soil chemical processes is in its infancy and there is a veritable need for much future research.

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**References**


