

TECHNICAL REPORT

Measuring and Predicting the Natural and Enhanced Rate and Capacity of Abiotic Reduction of Munition Constituents

Determining Properly Normalized Second Order Rate Constants and Reactive Reductant Concentrations: Limited Reductant Kinetic Experiments

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Introduction

The reaction that takes place during the abiotic reduction of a contaminant N , e.g. a nitro aromatic compound (NAC), by a reductant R , e.g. a quinone, is assumed to be



where N^* and R^* are the reduced NAC and oxidized reductant species respectively. The kinetic model for this reaction is

$$\frac{dN(t)}{dt} = -k_R R(t) N(t) \quad (2)$$

where k_R is the second order rate constant, $R(t)$ is the reductant concentration, and $N(t)$ is the NAC concentration. The usual experimental method employed to obtain the second order rate constant is determine k_R in experiments where R is large enough so that it is constant at the initial condition $R(0)$ during the experiment. For this situation, the kinetic model (Eq.2) becomes

$$\frac{dN(t)}{dt} = -k_R R(0) N(t) \quad (3)$$

Defining the first order rate constant

$$k_{obs} = k_R R(0) \quad (4)$$

Eq.3 becomes

$$\frac{dN(t)}{dt} = -k_{Obs}N(t) \quad (5)$$

whose solution is

$$N(t) = N(0) \exp(-k_{Obs}t) \quad (6)$$

The reason for this experimental design is that the expected result (Eq.6) is an exponential decrease of $N(t)$. The first order rate constant k_{Obs} is obtained by fitting a straight line to $\ln(N(t))$ vs t which has slope $-k_{Obs}$.

The second order rate constant is found from the first order rate constant k_{Obs} using Eq.4

$$k_R = \frac{k_{Obs}}{R(0)} \quad (7)$$

This presumes that the concentration of the reductant $R(0)$ is known. For a single dissolved reductant, for example a single quinone, the concentration is known. However, the situation is different for other reductants of interest.

Complex Reductants

The kinetics of abiotic reduction where the reductant is complex, for example humic acid, can also be analyzed. Let HA be the concentration of humic acid used in the experiment. Eq.2 becomes

$$\frac{dN(t)}{dt} = -k_R N(t) HA(t) \quad (8)$$

where the experiment is performed such that $HA(t) = HA_0$ is constant. The second order rate constant is obtained using Eq.4

$$k_R = \frac{k_{Obs}}{HA_0} \quad (9)$$

The problem with this formulation is that only a fraction of the humic acid, e.g. the quinone functionalities, are the reductant R , and that fraction is not known. Therefore, k_R derived from Eq.9 is not the true second order rate constant, but rather a scaled first order rate constant k_{Obs} , scaled by a constant HA_0 . The next section presents a method to determine the proper second order rate constant and the reductant concentration.

Limited Reductant Experiment

Consider a kinetic experiment with initial concentrations of NAC $N(0) = N_0$ and reductant $R(0) = R_0$ where the initial reductant concentration is smaller than the initial NAC concentration in electron equivalents

$$R_0 < N_0 \quad (10)$$

so that at the termination of the experiment the NAC concentration is greater than zero. For this situation a kinetic equation for the reductant is also required since the reductant concentration $R(t)$ is changing in Eq.(2). A stoichiometric coefficient is also needed to account for the quantity of reductant required to reduce the NAC. Let ν be the quantity of reductant $R(t)$ required to reduce $N(t)$. Expressing the relationship between the rates of change of $R(t)$ and $N(t)$ yields

$$\frac{dR(t)}{dt} = \nu \frac{dN(t)}{dt} \quad (11)$$

For concentrations of N and R in mol/L, the units of ν can be found from the units of $dR(t)/dt$ and $dN(t)/dt$

$$\left(\frac{\text{mol } R}{L \text{ sec}} \right) = \nu \left(\frac{\text{mol } N}{L \text{ sec}} \right) \quad (12)$$

Therefore, ν has the units

$$\nu \left(\frac{\text{mol } R}{\text{mol } N} \right) \quad (13)$$

The units of the reaction rate constant k_R is

$$\frac{dN(t)}{dt} = -k_R R(t) N(t) \quad (14)$$

$$\left(\frac{\text{mol } N}{L \text{ sec}} \right) = -k_R \left(\frac{\text{mol } R}{L} \right) \left(\frac{\text{mol } N}{L} \right) \quad (15)$$

Therefore, the rate constant has units

$$k_R \left(\frac{L}{\text{mol } R \text{ sec}} \right) \quad (16)$$

Finally, the kinetic model for the reductant is

$$\frac{dR(t)}{dt} = \nu \frac{dN(t)}{dt} = -\nu k_R R(t) N(t) \quad (17)$$

The solution of Eq.(14) for $N(t)$ is obtained by using Eq. (11) to form the difference

$$\nu \frac{dN(t)}{dt} - \frac{dR(t)}{dt} = 0 \quad (18)$$

which does not change during the reaction since the right hand side of Eq.(18) equals zero. Integrating Eq.(18) yields

$$\nu N(t) - R(t) = \nu N_0 - R_0 \quad (19)$$

where N_0 and R_0 are used to denote $N(0)$ and $R(0)$ respectively. Solving Eq.(19) for $R(t)$

$$R(t) = \nu N(t) - \nu N_0 + R_0 \quad (20)$$

and substituting Eq.(20) into Eq.(14) yields

$$dN(t)/dt = -k_R N(t) [\nu N(t) - \nu N_0 + R_0] \quad (21)$$

The solution is found by direct integration

$$\int_{N_0}^{N(t)} \frac{dN(t)}{-k_R N(t) [\nu N(t) - \nu N_0 + R_0]} = \int_0^t dt \quad (22)$$

to yield

$$N(t) = \frac{N_0 (N_0 \nu - R_0)}{N_0 \nu - R_0 \exp(-(N_0 k_R \nu t - R_0 k_R t))} \quad (23)$$

The first order reaction rate constant is the initial slope of $\ln(N(t)/N_0)$ and it can be found using a Taylor series expansion of Eq.(23) in time t

$$\ln(N(t)) = \ln(N_0) - k_R R_0 t + \dots \quad (24)$$

i.e. $k_R R_0$.

Eq.(23) can be expressed in dimensionless form

$$\frac{N(t)}{N_0} = \frac{\left(1 - \frac{R_0}{\nu N_0}\right)}{1 - \frac{R_0}{\nu N_0} \exp\left(-\left(\frac{\nu N_0}{R_0} - 1\right) k_R R_0 t\right)} \quad (25)$$

where normalized NAC concentration $N(t)/N_0$ is decreasing as dimensionless time $k_R R_0 t = k_{Obs} t$ increases. The extent of the decline is determined by the ratio of reductant to NAC concentration $R_0/\nu N_0$.

A dimensionless log-linear plot of $N(t)/N_0$ versus $k_R R_0 t$ for various concentrations of normalized initial reductant $R_0/\nu N_0$ using Eq.(25) are presented in Fig.1. As $R_0/\nu N_0$ is increased from $R_0/\nu N_0 = 0.1$ to $R_0/\nu N_0 = 0.9$ an increasing fraction of the initial concentration is reduced. The dashed line is the exponential solution (Eq.24). The initial portion of each curve is tangent to that line and then deviates as the reductant concentration decreases from its initial concentration R_0 .

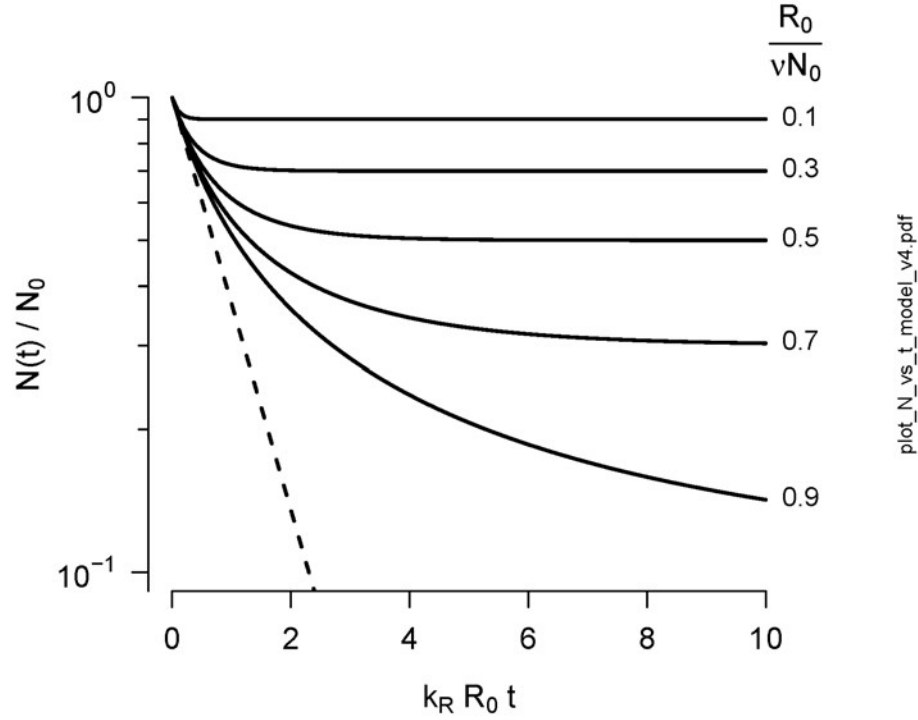


Figure 1: Example solutions. Log-linear plot of $N(t)/N_0$ vs $k_R R_0 t$ for $R_0/vN_0 = 0.1, \dots, 0.9$ (Eq.25). Dashed line is the exponential solution (Eq.24).

Stoichiometric Coefficient

The stoichiometric coefficient ν is a parameter in the kinetic model (Eq.25). For an MC whose extent of reduction is unknown, the stoichiometric coefficient would need to be determined separately. However Eq.(25) can still be used. Making the substitutions

$$R'_0 = \frac{R_0}{\nu} \quad (26a)$$

$$k'_R = \nu k_R \quad (26b)$$

yields

$$\frac{N(t)}{N_0} = \frac{\left(1 - \frac{R'_0}{N_0}\right)}{1 - \frac{R'_0}{N_0} \exp\left(-\left(\frac{N_0}{R'_0} - 1\right) k'_R R'_0 t\right)} \quad (27)$$

The parameters R_0' and k_R' have the units

$$R_0' = \frac{R_0}{\nu} = \left(\frac{\text{mol } R}{L} \right) / \left(\frac{\text{mol } R}{\text{mol } N} \right) = \left(\frac{\text{mol } N}{L} \right) \quad (28)$$

$$k_R' = \nu k_R = \left(\frac{\text{mol } R}{\text{mol } N} \right) \left(\frac{L}{\text{mol } R \text{ sec}} \right) = \left(\frac{L}{\text{mol } N \text{ sec}} \right) \quad (29)$$

It is clear that R_0' and k_R' are the initial reductant concentration in NAC equivalents and second order reaction rate constant (Eqs.28 and 29). They can be used to characterize the rate and reductant quantities that fit the experimental data. They can also be expressed in the original units when the stoichiometric coefficient is determined by solving Eqs.(26) for the parameters in reductant concentrations

$$R_0 = \nu R_0' \quad (30a)$$

$$k_R = \frac{k_R'}{\nu} \quad (30b)$$

It is also important to note that the first order reaction rate constant (Eq.4) can be computed using the NAC equivalent parameters Eq.(30)

$$k_{Obs} = k_R R_0 = \left(\frac{k_R'}{\nu} \right) (\nu R_0') = k_R' R_0' \quad (31)$$

Applications

Consider a set of experiments where the initial NAC concentration N_0 is constant and the concentration of the reductant R_0 is varied: $R_{0,1}$, $R_{0,2}$, and $R_{0,3}$, all of which are small enough to leave a residual NAC concentration at the end of the reaction. These are limited reductant experiments. For example, R_k , $k = 1, 2$ and 3 are reductant concentrations of increasingly reduced humic acid (HA) produced by adding increasing concentrations of dithionite to a constant concentration of humic acid. The kinetic model, Eq.(25), requires the initial concentrations of the reactive reductant components, $R_{0,1}$, $R_{0,2}$, and $R_{0,3}$, and the second order rate constant k_R . The stoichiometric coefficient ν is also necessary. It is the ratio of the quantity of electrons required to reduce the NAC to the quantity of the electrons donated by the reductant in the proper units for each. The remaining 4 parameters $R_{0,1}$, $R_{0,2}$, $R_{0,3}$, and k_R are obtained by fitting Eq.(25) to the experimental data using Solver in Excel. As shown above, the kinetic model can be applied using the NAC normalized parameters $R_{0,1}'$, $R_{0,2}'$, $R_{0,3}'$, and k_R' (Eq.27).

Two examples of limited reductant kinetic experiments are presented below. The first is the reduction of nitrobenzene by Leonardite humic acid (LHA). Three increasing quantities of sodium dithionite [$Na_2S_2O_4$] = 561,799 and 893 $\mu\text{mol/g}$ LHA were added to 0.1 g LHA/L to produce successfully more reduced LHA. The results are shown in Fig.2.

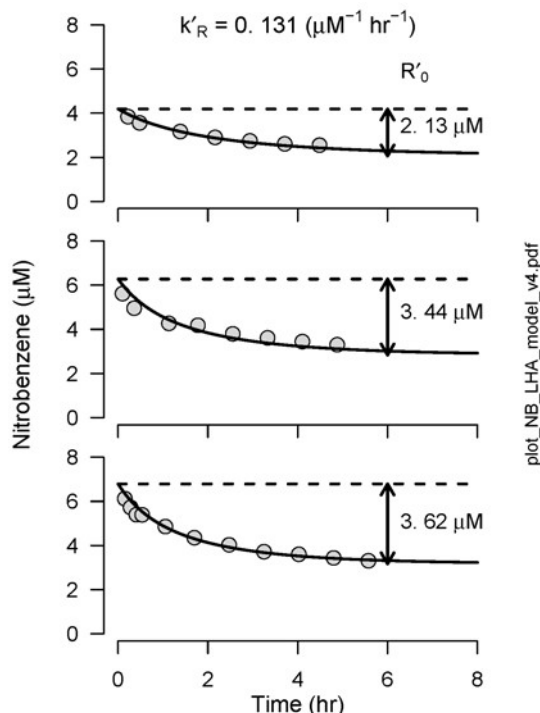


Figure 2: Reduction of nitrobenzene (NB) by Leonardite humic acid reduced by adding [$Na_2S_2O_4$] = 561,799, and 893 $\mu\text{mol/g}$ LHA to 0.1 g LHA/L. Plot of experimentally determined NB concentrations (symbols) and the kinetic model Eq.(27) $N(t)$ versus time t (lines). The NAC equivalent second order rate constant k'_R and reductant quantities R'_0 are listed.

The parameters were estimated by fitting Eq.(27). The fact that a single second order rate constant applies to the three reductant concentrations is interesting and suggests that the fitted k'_R is an average of the span of second order rate constants for the functionalities in the HA that are reducing nitrobenzene. The first order rate constants for the three cases are $k_{obs} = 0.279, 0.450, 0.474 \text{ hr}^{-1}$.

The second example, Fig.3, is NTO (3-nitro-1,2,4-triazol-5-one) reduced by ferrous iron (Fe^{II}) in the presence of hematite (Fe_2O_3). Three additions of Fe^{II} :

$[\text{Fe}^{\text{II}}] = 160, 480, 960 \mu\text{mol/g Fe}_2\text{O}_3$ are added to a 1.0 g $\text{Fe}_2\text{O}_3/\text{L}$ suspension. As in the case of the LHA, a single second order rate constant fits the data with reductant concentration R'_0 increasing as increasing concentrations of Fe^{II} are added. The first order rate constants for the three cases are $k_{\text{Obs}} = 0.0407, 0.0453, 0.254 \text{ hr}^{-1}$.

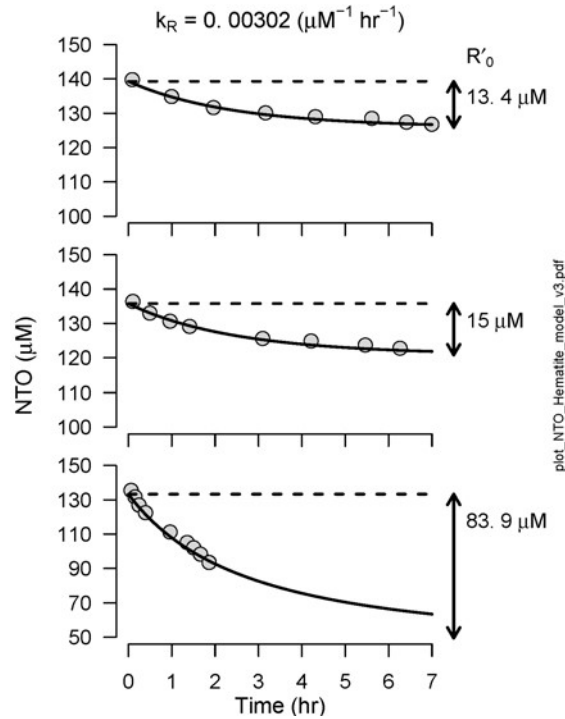


Figure 3: Reduction of 3-nitro-1,2,4-triazol-5-one (NTO) by hematite reduced by adding $[\text{Fe}^{\text{II}}] = 160, 480, 960 \mu\text{mol/g Fe}_2\text{O}_3$ to a 1.0 g $\text{Fe}_2\text{O}_3/\text{L}$ suspension. Plot of experimentally determined NTO concentrations (symbols) and the kinetic model Eq.(27) $N(t)$ versus time t (lines). The NTO equivalent second order rate constant k'_R and reductant quantities R'_0 are listed.

Summary

An experimental methodology utilizing limited reductant kinetic experiments is proposed that can be analyzed using the solution (Eq.25 or 27) of the kinetic Eqs.14 and 17. The results are second order rate constants and the quantity of reductant available at the experimental conditions of the

reaction. These parameters can then be used to investigate which of the experimental conditions are affecting magnitude of the second order rate constant, the reductant concentrations and the resulting first order rate constant.

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