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Predicting the Rate Constants of Munition Compound Reduction by the Fe(II)-Hematite and Fe(II)-Goethite Redox Couples

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Production, use, and disposal of munition compounds (MCs) have resulted in widespread contamination of soil and groundwater. Abiotic reduction by redox-facile soil constituents such as iron minerals is an important fate process for MCs. Understanding these reactions is important for evaluating the environmental fate of MCs and for remediating MC-contaminated sites. Therefore, in this study, we performed batch kinetic experiments to measure the reduction rate constants of three groups of MCs, such as poly-nitroaromatics (2,4-dinitroanisole (DNAN) and 2,4,6-trinitrotoluene (TNT)), nitramines (1,3,5-trinitro-1,3,5-triazinane (RDX) and nitroguanidine (NQ)), and azoles (3,4-dinitropyrazole (DNP) and 3-nitro-1,2,4-triazol-5-one (NTO)) by Fe^{2+}_{aq} in the presence of hematite or goethite. The reactivity of the MCs spanned nearly six orders of magnitude, following the order: DNP^- > NTO^- >TNT > DNAN > RDX > NQ. Results showed that the surface area normalized reduction rate constants (k_{SA}) scaled with compound reducibility (i.e., aqueous-phase one electron reduction potential, E_H^1) and the thermodynamic state of the iron oxide-Fe^{2+} redox couple (i.e., the strength of the reductant, pH+pe). As a result, a linear free energy relationship (LFER) was obtained for the prediction of the measured reduction rate constants of MCs by iron oxides-Fe^{2+} redox couples. The finding that the k_{SA} of MCs can all be described by a single LFER of the form of $\log(k_{SA}) = 1.12 \pm 0.04\ (0.53E_H^1 - \text{pH+pe}) + 5.52 \pm 0.23$, implies that these structurally diverse MCs are reduced by iron oxides-Fe^{2+} redox couples through the same mechanism involving a common rate-limiting step. The results enhance our ability to predict the reduction rates of a broad range of legacy and emerging MCs and related nitro compounds and shed light on the common mechanism and rate-limiting step for nitro reduction reactions by iron oxides-Fe^{2+} redox couples.