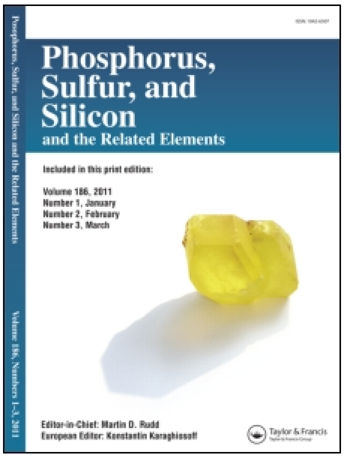

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Effects of Divalent Metal Ions on pH-Dependent Hydrolysis of *p*-Nitrophenyl (*E*)-(Hydroxyminio) Phosphonoacetate

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Effects of Divalent Metal Ions on pH-Dependent Hydrolysis of *p*-Nitrophenyl (*E*)-(Hydroxyimino)Phosphonoacetate

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The (*E*)-oxime of phosphonoglyoxylic acid, or (*E*)-troika acid [(*E*)-**1**] undergoes fragmentation leading to phosphorylation of the aqueous solvent at neutral pH and room temperature.[1] In contrast, the corresponding C-methyl ester (*E*)-**2** is stable under these mild conditions. Conversion of the unreactive (*E*)-**2** to (*E*)-**1** requires demethylation a pH 13–14, generating the polyanion of (*E*)-**1**, which becomes reactive on protonation.[1]

The C-*p*-nitrophenyl ester of (*E*)-**1**, (*E*)-**3**, is expected to be more readily hydrolyzed at moderately alkaline pH, and also provides a standard chromophore facilitating kinetic studies. The rate of *p*-nitrophenoxide release from (*E*)-**3** was examined as a function of pH, temperature and added divalent metal ion (Mg^{2+}, Ca^{2+}, Ni^{2+}) concentration. In contrast to the corresponding unmodified phosphonoacetate ester (**4**),[2] (*E*)-**3** (0.01 M borate, pH 8.5, 25 °C) hydrolyzed more rapidly than *p*-nitrophenyl acetate. At 50 °C, $\log(k_{obsd})$ for hydrolysis of (*E*)-**3** was ~pH-independent from pH 4–7 but correlated with [OH^-] from pH 7.2 to at least pH 8.7. At 25 °C, the correlation with [OH^-] could be observed at pH 8.5–10.5. Ni^{2+} (10 mM, 50 °C, est. 80% saturation) accelerated hydrolysis of (*E*)-**3** by OH^- almost 10^3x, shifting the start of the pH-dependent phase to pH ~4.5. Added 10 mM Mg^{2+} or Ca^{2+} had only weak effects. In view of the known affinity of oximes for transition metal cations, the pronounced rate acceleration by Ni^{2+} presumably involves coordination by the oximino group of (*E*)-**3**. The results demonstrate specific metal-promoted hydrolysis of a susceptible troika acid C-ester as a new modality for induced phosphorylation under mild aqueous conditions.

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