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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 at 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 (Mg²⁺, Ca²⁺, Ni²⁺) 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. Ni²⁺ (10 mM, 50 °C, est. 80% saturation) accelerated hydrolysis of (*E*)-3 by OH⁻ almost 10³x, shifting the start of the pH-dependent phase to pH ~4.5. Added 10 mM Mg²⁺ or Ca²⁺ had only weak effects. In view of the known affinity of oximes for transition metal cations, the pronounced rate acceleration by Ni²⁺ 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.

References

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