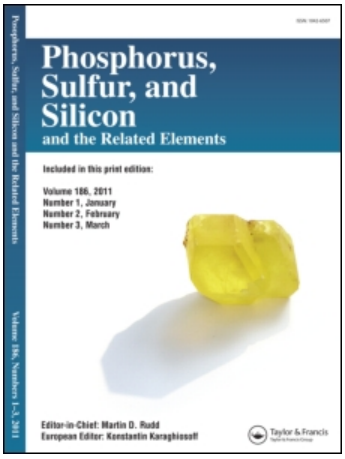

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KINETICS AND MECHANISMS OF THE PERMANGANATE ION OXIDATION OF 2-THIOURACILS

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KINETICS AND MECHANISMS OF THE PERMANGANATE ION OXIDATION OF 2-THIOURACILS

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Permanganate ion rapidly oxidizes 2-thiouracils (2,3-dihydro-2-thioxo-4-(1H)-pyrimidinones, 4-hydroxy-2-pyrimidinethiols) to the corresponding uracil-2-sulfonates. The reaction is first order in oxidant and first order in reductant. Relatively small energies of activation and relatively large negative entropies of activation are observed. Substitution of alkyl groups at positions 1,3, and 6 influences the rate of oxidation. Preliminary studies suggest that the overall oxidation mechanism could involve sulfenic acid and sulfinic acid, and that the initial step could involve the thiol group, thiolate anion, or thiocarbonyl group. These and other possible mechanisms will be discussed.