

II. Reaction Mechanism

The mechanism proposed in Scheme 1 for reaction of an *N*-hydroxypyridine-2-thione ester is supported by a number of experimental observations. The carbon-centered radical $R\cdot$ is detectable by ESR spectroscopy,⁹ and flash photolysis experiments identify the 2-pyridylthiyl radical ($PyS\cdot$) as one of the transients formed by ester photolysis.^{10,11} Also, the radical-chain nature of the reaction is attested to by quantum yields that range between 6 to 35, depending upon the reaction conditions.¹²

There are several characteristics of reactions of *N*-hydroxypyridine-2-thione esters that have “come to light” as a result of mechanistic studies. One of these is that addition of $R\cdot$ to the carbon–sulfur double bond is reversible (Scheme 1).¹³ Another is that the 2-pyridylthiyl radical, produced by photolysis in the first initiation step (Scheme 1), can add to a molecule of the starting ester in the second initiation step to provide another pathway for acyloxy radical formation.¹⁴

Several factors contribute to the driving force for the rate-determining step in the reaction shown in Scheme 1. One of these is conversion of a nonaromatic starting material into an aromatic product.^{15,16} Another is that a weak N–O bond (BDE = 43 kcal mole⁻¹)¹⁷ in the substrate is being replaced with a stronger N–C bond (BDE \cong 76 kcal mole⁻¹ for the second bond between carbon and nitrogen atoms)¹⁸ in the product.

This page titled [II. Reaction Mechanism](#) is shared under a [All Rights Reserved \(used with permission\)](#) license and was authored, remixed, and/or curated by [Roger W. Binkley and Edith R. Binkley](#).