The reactions of methylrhenium trioxide (MTO) with hydrogen peroxide have been characterized. Specifically MTO will use hydrogen peroxide as an oxygen donor once to form product A with one cyclic Re-O-O moiety \([\text{H}_3\text{C-}\text{ReO}_2(\eta^2-\text{O}_2)]\), and twice to form product B with two of the cyclic moiety \([\text{H}_3\text{C-}\text{Re(O)(\eta^2-\text{O}_2)}_2]\). In basic conditions MTO will react with OOH and product A will react with OH\(^-\) to form methanol and perrhenate ion \((\text{ReO}_4^-)\). When considering all of the reactions, the lowest energy path is the reaction of MTO with OOH\(^-\) with a maximum barrier height of 22.2 kcal mol\(^{-1}\). The barrier heights for formation of product A, product B and methanol via product A are 27.4, 30.6 and 32.5 kcal mol\(^{-1}\) respectively.