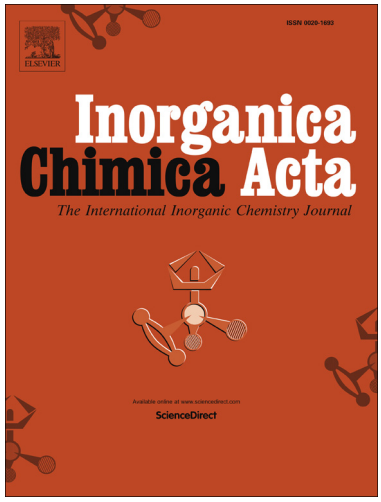

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Abstract

Ketenes are interesting reactive intermediates that find a wide range of synthetic applications. Density functional theory calculations at the MO6/LACVP*and B3LYP/LACVP* levels of theory have been employed to explore the peri-, chemo- , and regio- selectivity of the addition of manganese oxo complexes MnO_3L (L = Cl, O^-, OCH_3, CH_3) to substituted ketenes $O=C=C(CH_3)(X)$ [X = H, CH_3, Cl, CN, Ph] with the aim of elucidating the effects of substituents on the mechanism of the reactions. The results show that the concerted [3 + 2] addition of the C=C bond of the ketene across the metal complex is the most preferred pathway in all the reactions studied (with respect to changing ligand L on the metal complex or substituent X on the ketene) except in the reaction of MnO_4^- (i.e. for L = O^-) with dimethyl ketene, which follows only a stepwise addition pathway. [2 + 2] addition is found to be possible only in the reaction of MnO_3-OCH_3 with dimethyl ketene where the activation barrier for $[2 + 2]_{C=O}$ addition is 23.79 kcalmol, which is far greater than the barrier for the [3 + 2] addition. The reactions of dimethyl ketene with MnO_4^- will most likely lead to the formation of an ester precursor and the reaction of MnO_3Cl with the substituted ketenes would lead to the formation of an ester precursor, chlorohydrin precursor, acetaldehyde and carbon monoxide (for X = H, Cl). Generally, reactions involving an increase in oxidation state of metal have higher activation barriers. For both [3 + 2] and [2 + 2] addition, low activation barriers are obtained when the substituent on the ketene is electron-donating while high activation barriers are obtained when the substituent is electron-withdrawing. The reactions of ketenes with MnO_3L complexes have lower activation barriers for the preferred [3 + 2] and [2 + 2] addition pathways as well as fewer side reactions than those of the ReO_3L complexes reported in the literature, a trend which was seen in our earlier work with reactions of group VII metals with olefins, implying that manganese oxo complexes efficiently and selectively catalyze specific reactions in oxidation of ketenes and olefins than do Re oxo complexes and therefore Mn oxo complexes may be better catalysts for specific oxidation reactions of ketenes and olefins than Re complexes are.