C-C versus C-H Bond Activation of Alkynes by Early Second Row Transition Metal Atoms

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ABSTRACT

The reactions of Y (a^2D), Zr (a^3F), Nb (a^6D), Mo (a^7S) and excited-state Mo* (a^5S) with propyne (methylacetylene) and 2-butyne (dimethylacetylene) were investigated using crossed molecular beams. For reactions with propyne, non-reactive scattering and H\textsubscript{2} elimination (forming MC\textsubscript{3}H\textsubscript{2}) were observed for each metal atom reactant. For Y + propyne, an additional product channel (YCCH + CH\textsubscript{3}) associated with sp\textsuperscript{3}-sp C-C bond cleavage was observed. The branching ratio between CH\textsubscript{3} and H\textsubscript{2} elimination, \(\phi_{YC2H} : \phi_{YC3H2}\), increased from 0.00 : 1.00 at a collision energy (\(E_{coll}\)) of 13 kcal/mol to 0.11 : 1.00 at 24 kcal/mol. The measured threshold for the onset of CH\textsubscript{3} elimination was in good agreement with our previous determination of D\textsubscript{0}(Y-CCH). For Y + 2-butyne, three competing product channels were observed at \(E_{coll} = 16\) and 28 kcal/mol: YC\textsubscript{4}H\textsubscript{4} + H\textsubscript{2}, YC\textsubscript{3}H\textsubscript{3} + CH\textsubscript{3} and YC\textsubscript{3}H\textsubscript{2} + CH\textsubscript{4}. While \(H\textsubscript{2}\) elimination was always dominant, the C-C bond cleavage products accounted for 21\% and 27\% of the total product signal at \(E_{coll} = 16\) and 28 kcal/mol, respectively. For Zr and Nb + 2-butyne, competition between \(H\textsubscript{2}\) and \(CH\textsubscript{4}\) elimination was observed, with C-C bond cleavage products accounting for 12\% and 4\% of the total product signal at \(E_{coll} = 16\) kcal/mol, respectively. For Mo and Mo* + 2-butyne only \(H\textsubscript{2}\) elimination was detected.