Determining Initial Rates

Determining initial rates (slopes) of a curved decay can be a tricky undertaking because a linear fit to such a curve is strongly dependent on the selected region. The tighter the selected region (i.e. closer to the zero time point), the better the theoretical read of the initial rate but the greater the noise due to the limited sample points. If the selected region extends farther out the time axis the signal-to-noise will improve, but the reading of the initial rate will be worse.

This problem can be avoided by fitting a significant part of the decay to a third-order polynomial ($at^2 + bt + c$). Be sure not to include too much curvature or the function will no longer fit well. The parameter $b$ represents the rate at time=zero (one may verify this by taking the first derivative with respect to t and setting $t=0$. Initial rate= $f'(0) = b$).

Prior to this analysis, be sure to convert your experimental observable (NMR intensity, IR absorbance etc.) to concentration to ensure a valid comparison between initial rates of varying concentrations and/or experimental conditions.