

Structure-reactivity correlation in the reactions of pyrrolidine with O-ethyl S-aryl dithiocarbonates in aqueous ethanol

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Abstract

The reactions of pyrrolidine with O-ethyl S-(X-phenyl) dithiocarbonates (X = 4-methyl, 4-methoxy, H, 4-chloro, 4-nitro, 2,4-dinitro, and 2,4,6-trinitro) are subjected to a kinetic study in 44 wt% aqueous ethanol, 25.0°C, and ionic strength 0.2 M (maintained with KCl). Pseudo-first-order kinetics are found under amine excess. Linear plots of the pseudo-first-order rate coefficient against concentration of free-base pyrrolidine are obtained for all the reactions, the nucleophilic rate coefficient (k_N) being the slope of such plots. The Bronsted-type plot ($\log k_N$ vs. pK_a for the leaving group) is linear with slope $\beta_{lg} = -0.2$, which is consistent with a mechanism through a tetrahedral intermediate (T_{\pm}) where its formation is rate determining. The β_{lg} value is very similar to that found in the same reactions in water. There is a great difference in the mechanism of the reactions of O-ethyl S-phenyl dithiocarbonate with pyrrolidine (order one in amine) and piperidine (complex order in amine) in aqueous ethanol, and this is attributed to a greater nucleofugality from T_{\pm} of piperidine rather than pyrrolidine. © 1997 John Wiley & Sons, Inc..