



Figure 1. Brønsted-type plot for Michael-type additions of $Z\text{-C}_6\text{H}_4\text{NH}_2$ to 3-buten-2-one in H_2O at 25.0 ± 0.1 °C.

ated aniline in D_2O was found to be more reactive than aniline in H_2O , resulting in an inversed KIE ($k_N^{\text{H}}/k_N^{\text{D}} = 0.92$). The inversed KIE clearly suggests that the proton transfer is not involved in the rate-determining step but occurs rapidly after the rate-determining step. Accordingly, one can exclude TS1 and TS3, and the remaining TS2 is considered to be the most plausible transition state in the present reaction system.

In order to obtain more information on the reaction mechanism as well as the structure of the transition state, a Brønsted-type plot was constructed. As shown in Figure 1, the logarithmic second-order rate constants ($\log k_N$) are linearly correlated with the $\text{p}K_a$ values of the conjugated acids of anilines. A linear Brønsted-type plot indicates that there is no mechanism change upon changing the basicity of the nucleophiles, while a break or a curvature in a Brønsted-type plot is suggestive of a change in the reaction mechanism or in the rate-determining step of a multistep reaction.¹² Therefore, one can suggest that the reaction mechanism does not change upon changing the basicity of ArNH_2 in the present system, *i.e.*, the transition state is similar to TS2 and the rate-determining step is the k_1 step in Scheme 1.

The magnitude of β_{nuc} values has been suggested to represent relative degree of bond formation between the substrate and nucleophiles or relative degree of charge development on the nucleophilic atom at the rate-determining transition state.¹² The β_{nuc} value in the present system has been calculated to be 0.51, which is much larger than the one obtained from the reaction of **1** with RNH_2 ($\beta_{\text{nuc}} = 0.32$).^{5a} Therefore, one can suggest that the degree of bond formation between the substrate and nucleophile or the degree of positive charge developed on the nitrogen atom of amines is more significant for the reaction with ArNH_2 than with RNH_2 .

The magnitude of β_{nuc} values has been also used as a measure of the selectivity parameter.¹²⁻¹⁴ It has been generally

known that more reactive reaction system results in smaller β_{nuc} value for a variety of reactions and vice versa. Therefore, the reactivity-selectivity relationship has been accepted as a principle.^{13,14} However, this principle is no longer regarded as general because many exceptions have been found.^{13,14} In fact, ArNH_2 is found to be more reactive than RNH_2 in the reaction with **1**. Since the more reactive ArNH_2 results in a larger β_{nuc} value than the less reactive RNH_2 , the reactivity-selectivity principle is not valid in the present system.

In conclusion, enaminones **2** can be prepared quantitatively from the reaction of **1** with ArNH_2 without general base catalysis. The enaminone formation reaction proceeds stepwisely through TS2 and the rate-determining step is the k_1 step. The reactivity-selectivity principle is not valid in the reactions of **1** with ArNH_2 and RNH_2 .

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