

## Observation of Negative Activation Enthalpy in Amine Conjugate Addition to $\pi$ -Conjugated Molecules

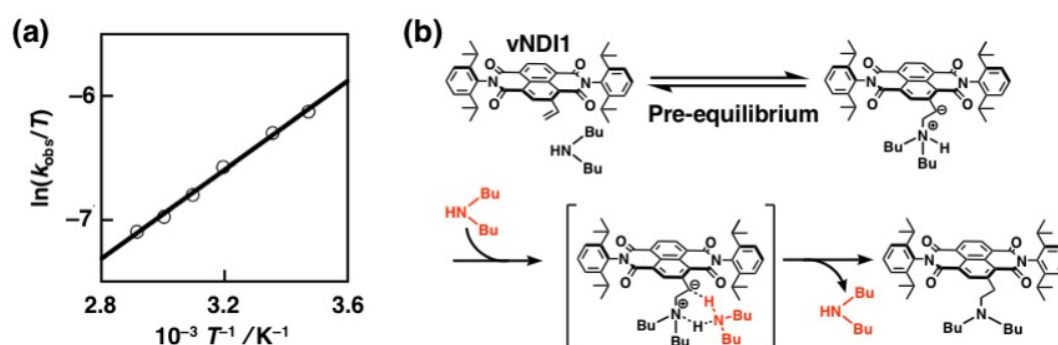
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Amine conjugate addition to alkenes activated by an electron-withdrawing group has been widely used to prepare N-atom containing functional molecules. Recently, we have found novel amine conjugate addition of electron-withdrawing  $\pi$ -conjugated molecules such as naphthalenediimide (NDI) that proceeds rapidly in quantitative yields to afford amino-functionalized  $\pi$ -systems.<sup>1)</sup> However, the reaction mechanism of why such reactions of  $\pi$ -conjugated molecules proceed so efficiently is not fully scrutinized.

In this work, we systematically investigated the reaction mechanism of amine conjugate addition using several vinyl-group appended  $\pi$ -conjugated molecules. We found that the reaction of large  $\pi$ -conjugated molecules like a vinyl-substituted NDI (**vNDI1**) with dibutylamine exhibited unusual negative temperature dependence in polar solvents: the lower the temperature, the faster the rate. Eyring plot afforded the negative activation enthalpy ( $-15.0 \text{ kJ mol}^{-1}$ ) in 1,2-dimethoxyethane (**Fig. 1a**), indicating the existence of pre-equilibrium reaction that forms a stable complex.<sup>2)</sup> The detail spectroscopic and theoretical analyses of the reaction mechanism revealed that two amine molecules are involved in the reaction, one of which acts as an internal catalyst, as shown in **Fig. 1b**. We infer that the stabilization of the intermediate complex by the resonance structure of the  $\pi$ -system is the key to the efficient amine conjugate addition.



**Fig. 1** (a) Eyring plot of the reaction of **vNDI1** with dibutylamine in 1,2-dimethoxyethane. (b) Plausible reaction mechanism of amine conjugate addition to **vNDI1**.

1) H. Sanematsu, *et al. Chem. Eur. J.* **2021**, 27, 934. 2) J. G. Miller, *et al. J. Am. Chem. Soc.* **1975**, 97, 4036.