some through the hydrophobic interactions[15]. The conclusive two remarks for this experiment are following;

1) the binding sites of c-AMP and estriol to phytochrome are different, (the fromer is a hydrophilic domain and the latter is the chromophore binding site-a hydrophobic domain)

2) both receptors can bind more preferentially to the Pfr form of phytochrome than to the Pr form.

When we combine this result with the one[15] suggesting us that receptor-phytochrome complexes incorporate better into the liposome than the one of free phytochrome, one of the roles of c-AMP and estriol in the photomorphogenic process would be speculated to be the enhancement of phytochrome binding to the membrane by the complexation.

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Substituent Effects on the Hydration Reactions of Dihydronicotinamides

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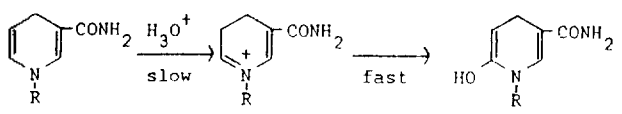
Reduced form of nicotinamide adenine dinucleotide (NADH) and its phosphate derivative (NADPH) are coenzymes for many dehydrogenases. In recent years various NAD(P)H model compounds, mainly 1,4-dihydronicotinamides (3-carbamoyl-1,4-dihydropyridines), were utilized in exploring the reactions and mechanisms involving the coenzymes and also in variety of synthetic reactions.[1] Dihydronicotinamides reduce various unsaturated funtionalities, transfer nucleophiles to substrates, and are used for recycling NAD(P)H in NAD(P)H dependent enzyme-catalyzed organic synthesis.[2] Meanwhile, dihydronicotinamides as well as NAD(P)H are known to be unstable in acidic medium and undergo acid catalyzed hydration reaction.[3-9]



1 **2** **3**

This deters the effectiveness of the compounds in various applications in organic reactions. In this communication we wish to report the results of kinetic studies on the hydration reactions of 1-aryl-1,4-dihydronicotinamides, which show great sensitivity of the reaction rate on the nature of 1-substituents.

1-aryl-1,4-dihydronicotinamides were prepared by reduction of the corresponding 1-aryl-3-carbamoylpyridinium salts, which were obtained by reaction between 1-(2,4-dinitrophenyl)-3-carbamoylpyridinium salts with the corresponding aniline derivatives as described elsewhere.[10] Kinetic studies were performed in 2% 2-propanol-water medium containing a desired HCl concentration (5×10^{-5}M ~0.1 M) depending on the substituents of dihydronicotinamides. The reactions were followed by decrease in the absorbance of the characteristic absorption of dihydronicotinamides at 345-365 nm. The reactions were first order with respect to both the substrate and H^+.[11] This is in good agreement with the results on other dihydronicotinamides.[7,8] The second order rate constants k_H are summarized in Table 1.

It is evident from Table 1 that k_H becomes greater as the substituent at 1-position of dihydronicotinamide has greater electron-donating power. This agrees well with the conclusion that protonation of 1,4-dihydronicotinamide is involved in the rate-determining step[6-8], since the formation of iminium salts **2** would be more easily formed as electron density on the ring nitrogen is greater.

To correlate the hydration rate constants with character of 1-substituents of the dihydronicotinamides, the Hammett plots were made in Figure 1. The plots of log k_H for the hy-

Table 1. Second Order Rate Constants for Hydration Reactions of Dihydronicotinamides in 2% 2-propanol-water at 30°C

Compds.	R	λ_{max}/nm	k_H/M sec
1a	$C_6H_5CH_2$-	354	18
1b	4-$MeOC_6H_4$-	359	1.7
1c	4-MeC_6H_4-	355	1.5
1d	4-EtC_6H_4-	350	1.4
1e	C_6H_5-	363	1.1
1f	4-ClC_6H_4-	348	0.43
1g	4-NCC_6H_4-	358	0.039

λ_{max} are absorption maxima of each substrates and the kinetics were followed at these wavelengths.

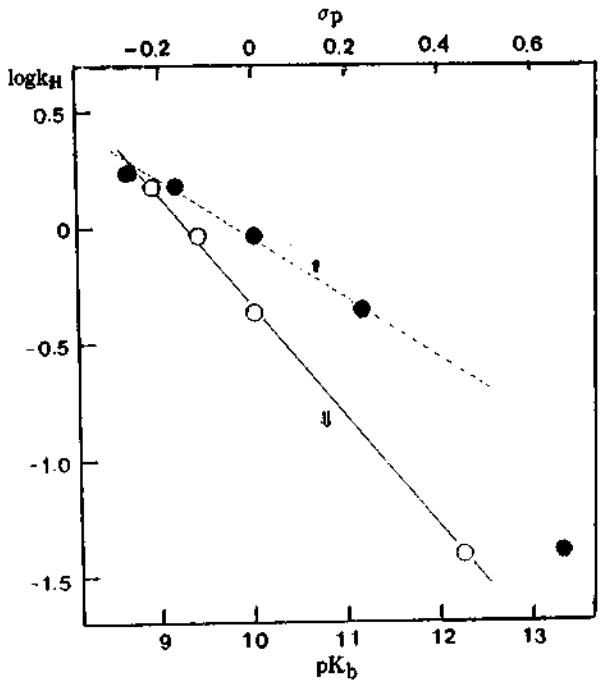


Figure 1. Hammett plots of log k_H for the hydration reaction of 1-substituted (XC_6H_4-)-1,4-dihydronicotinamides against σ_p (-●-) of the substituents(X) and pK_b (··○··) of the corresponding anilines($XC_6H_4NH_2$).

dration reaction of 1-substituted (XC_6H_4-)-1,4-dihydronicotinamides against σ_p of the substituent(X) and pK_b of the corresponding anilines ($XC_6H_4NH_2$) showed good linear relationships with the reaction constants of −1.3 (for σ_p) with the exception of X = CN, and −0.47 (for pK_b). This reaffirms the critical role of lone-pair electron density on the ring nitrogen on the hydration reactions.

There are reports that the reducing power of 1-substituted-1,4-dihydronicotinamides is similarly correlated with the electron-donating ability of the 1-substituents, i.e., lone-pair electron density on the ring nitrogen, of the reactants.[2,12] The fact that both the hydration of and reduction by dihydronicotinamides are facilitated by electron-donating substituents on the ring nitrogen imposes severe limitation upon the utility of the compounds as reducing agents. Therefore it is desirable to suppress the hydration reaction when one uses dihydronicotinamide as a reducing agent. One possible choice for this is to carry out the reduction in nonaqueous media or at high pH, but this may not be applicable for some cases. It is noteworthy that in our preliminary study the metal ions such as Mg^{++} and Zn^{++} which are known to exhibit catalytic effect on the reduction reactions by dihydronicotinamides[13], moderately inhibit the hydration reaction. The works on this aspect are in progress.

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11. The pseudo first-order rate constants (k_ψ) were obtained from slopes of plots of ln ($A-A_\infty$) vs. time as described in Ref. 7. The k_H values were calculated by $k_\psi/[H^+]$ for at least four different HCl concentrations and agreed within 10%. The average values were listed in Table 1. Bunton *et al.*[8] showed that plots of k_ψ vs $[H^+]$ deviate from linearity at modeately high [HCl], e.g. [HCl]>0.1 M for **1a** (pKa = 0.87), probably due to formation of unreactive species by substrate protonation on the carbonyl group. The pKa's of **1b**-**1g** are expected to be smaller than 0.87 and thus formation of the unreactive species would be negligible in our experimental condition as aryl groups are more electron withdrawing than benzyl group. The observed good linearity between k_ψ and $[H^+]$ supports these.
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