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Coenzyme Models. XII. Kinetics and Mechanisms of 1,4-Dihydronicotinamide Reduction of Carbon-Carbon Double Bonds. Influence of Added Mg^{2+} Ion and Acetic Acid

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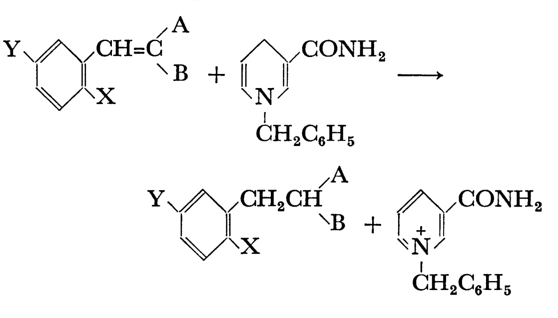
Nonenzymatic dihydronicotinamide reduction of carbon-carbon double bonds occurs with the aid of Mg^{2+} ion or acetic acid. The role of Mg^{2+} ion and acetic acid is discussed on the basis of spectral studies, kinetic measurements, and product analyses. The addition of Mg^{2+} ion caused the shift of the NMR peak of substrate α-proton to lower field, and the magnitude was parallel to the yield of reduced methylene derivatives. Kinetic studies suggested that the dihydronicotinamide reduction in the presence of Mg^{2+} ion is most reasonably understood by assuming a competitive complexation of dihydronicotinamide and substrate with Mg^{2+} ion. On the other hand, acetic acid aids the reduction by means of general acid catalysis, but an alternative mechanism is suggested for the reduction of benzylidenemalononitrile.

It has been established that the metal ion and the ortho hydroxyl group greatly assist the nonenzymatic dihydronicotinamide reduction of >C=O, >C=S, and >C=N double bonds.[1-3] The findings in nonenzymatic systems are considerably important in connection with the fact that most of NADH dependent enzymes employ metal ion (*e.g.*, Zn^{2+} ion) and/or Brönsted acid (*e.g.*, imidazolium ion) in the active sites.[4,5] From the mechanistic point of view, however, the reductions of these double bonds seem somewhat complicated because of (i) the possible interaction of substrates with the metal ion or the ortho hydroxyl group both in the initial state and in the transition state[6,7] and (ii) the equilibrium of substrate hydration which is catalyzed by acid and base.[8,9] In this respect, C=C double bonds are convenient substrates to assess the influence of added metal ions and Brönsted acids, since they are not subjected to hydration equilibria[10] and interact very weakly with added acids.[11]

We selected several styrene derivatives (Table 1) and performed the reduction by *N*-benzyl-1,4-dihydronicotinamide (BzlNicH) in a few solvents. The results are discussed on the bases of spectral studies, kinetic measurements, and product analyses.



(1)

Experimental

Materials. The following styrene derivatives were prepared according to the literature and identified by spectroscopic (NMR and IR) methods and elemental analysis: benzylidenemalononitrile (**1**), mp 83—85 °C (lit,[12] 87 °C); β-nitrostyrene (**2**), mp 57—59 °C (lit,[13] 58—59 °C); diethyl benzylidenemalonate (**3**), bp 132—133 °C/2 mmHg (lit,[14] 160—163 °C/7 mmHg); isopropylidene benzylidenemalonate (**4**), mp 80—84 °C (lit,[15] 80—84 °C); 3,β-dinitrostyrene (**$2NO_2$**), mp 122—124 °C (lit,[16] 125 °C). 2-Hydroxy-β-nitrostyrene (**2OH**) was prepared from nitromethane and salicylaldehyde according to the method of Gairand and Lappin.[13] The product is a mixture of yellow solid and black oil. The mixture was heated to 60—70 °C on a steam bath, and the oily layer was decanted. Recrytallization of the residual yellow solid from methanol and water gave yellow needles, mp 130—133 °C. IR: ν_{OH} 3460 cm^{-1}, $\nu_{C=C}$ 1620 cm^{-1}, nitro group 1330 cm^{-1}. Found: C, 58.06; H, 4.31; N, 8.46%. Calcd for $C_8H_7NO_3$: C, 58.17; H, 4.28; N, 8.48%. The preparation of *N*-benzyl-1,4-dihydronicotinamide (BzlNicH) was described.[17]

Product Analyses. 1.0 mmol of a substrate and 1.2 mmol of BzlNicH were dissolved in 10 ml of dry solvent (acetonitrile or methanol), and the solution was gently refluxed in the dark for 2 h. The reaction was also carried out in the presence of acid (1.4 mmol $Mg(ClO_4)_2$ or 1.0 M acetic acid). In order to evaluate the relative reactivity of substrates, the reaction period was unified in 2 h. The solvent was evaporated at room temperature *in vacuo*, the residue being extracted with aqueous HCl (0.1 M) and chloroform. The chloroform layer was separated, dried over Na_2SO_4, and evaporated to dryness. The sample thus obtained was subjected to the NMR analysis (JEOL JNM-MH-100; solvent, Me_2SO-d_6 or $CDCl_3$). The reduced compounds provided doublet (for **1** and **3**) or triplet (**2**, **2OH**, and **$2NO_2$**) peaks at around 3.3 ppm which are characteristic of product α-methylenes. The yield of the reduced products was determined from integral intensity of the peaks with acetone oxime as internal standard. The reaction was repeated two to four times and the average value is recorded in Table 2. The solid product from **1** was recrystallized from ethanol, which gave benzylmalononitrile in 42% yield; mp 88—91 °C (lit,[18] 87 °C).

In the presence of acetic acid, the yield of the reduced product was not improved largely by elongation of the reaction period. For example, the reaction with **2** in methanol–acetic acid (1.0 M) for 24 h gave corresponding reduced product in 26% yield. This is probably due to the competing decomposition of BzlNicH.

The analysis of by-products was carried out mainly by the mass spectroscopic method. Black, viscous oil recovered from the reaction of BzlNicH and **2** in acetonitrile gave a M^+ peak at 306. If the dimer of **2**, $(C_6H_5C_2H_3NO_2)_2$, is formed, the M^+ peak is expected at 300. The reaction of BzlNicH and **4** in acetonitrile resulted in reddish-yellow solid, and the peak of the dimer (462 for $[C_6H_5C_2H_2(COO)_2C(CH_3)_2]_2$) could not be found in the mass spectrum. These results indicate that the dimer is not contained in the recovered solid. Since the

IR spectrum of the oily product from **2** showed strong absorptions due to nitro group, the nitro group of **2** is not reduced by BzlNicH under the present reaction conditions. Further investigation of the by-products is now continued in our laboratory.

Kinetics. The kinetic measurements were carried out at 30 °C in dry acetonitrile or ethanol. The progress of the reaction was followed spectrophotometrically by monitoring the decrease in the absorption of BzlNicH at 380 nm. Since excess substrate was used in all the cases, the pseudo first-order behavior was observed except in the presence of acetic acid. The rate of disappearance of BzlNicH(v_{obsd}) in the presence of acetic acid (AcOH) is described by

$$v_{\text{obsd}} = -\frac{[\text{BzlNicH}]}{\mathrm{d}t} = v_{\text{r}} + k_{\text{d}}[\text{BzlNicH}][\text{AcOH}], \quad (2)$$

where k_{d} is the second-order rate constant for acid-catalyzed decomposition of BzlNicH and v_{r} is the disappearance rate of BzlNicH other than the acid-catalyzed decomposition. The k_{d} term was separately evaluated in the absence of substrate, and v_{r} was determined by substracting this value from v_{obsd}. The detail of the method has been described.[20]

Results and Discussion

Substituent Effect. The BzlNicH reduction of six styrene derivatives was carried out in acetonitrile or in methanol, and the yield of the reduced product was estimated by the NMR method (Table 2: for the detail of the method, see Experimental). The reaction rates were estimated from disappearance of the UV absorption band of BzlNicH at 30 °C, and the apparent second-order rate constants ($k_{\text{r}}=k_{\text{obsd}}$ (pseudo first-order rate constants)/[substrate]) are summarized in Table 3.

Table 1. Structure of substrates

Abbreviation	A	B	X	Y
1	CN	CN	H	H
2	NO_2	H	H	H
3	$COOC_2H_5$	$COOC_2H_5$	H	H
4[a]				
2OH	NO_2	H	OH	H
2NO₂	NO_2	H	H	NO_2

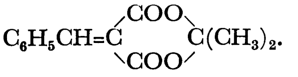
a) **4**, 
$C_6H_5CH{=}C\langle{}^{COO}_{COO}\rangle C(CH_3)_2$.

Table 3. Apparent second-order rate constants ($k_{\text{r}}\times 10^2$, $M^{-1}\,s^{-1}$) for the BzlNicH reduction and third-order rate constants ($k_{\text{AcOH}}\times 10^2$, $M^{-2}\,s^{-1}$) for added acetic acid[a]

Substrate	CH_3CN		C_2H_5OH	
	k_{r}	k_{AcOH}	k_{r}	k_{AcOH}
1	3.8	0	6.3	0
2	0.5	22.3	0	6.3
2OH	16.7		23.3	
2NO₂	6.0	18.3	0.5	2.7

a) 30° C, pH 8.5, μ=0.02 with KCl, [BzlNicH]=1.00×10^{-4} M, [substrate]=5.00×10^{-3} M.

As shown in Table 2, the reduction of **1** in methanol gave the corresponding reduced products in 10% yield. On the other hand, **2** was not reduced by BzlNicH under the similar reaction conditions. Base on the σ° value,[21] the C=C double bond of **1** is presumed to be more electron-deficient than that of **2** ($2\sigma^\circ_{\text{CN}}=1.12$, $\sigma^\circ_{\text{NO}_2}=0.63$), and is more sensitive to BzlNicH reduction. The electron-withdrawing group on benzene ring (*e.g.*, **2NO₂**) also enhanced the yield. Evidently, the BzlNicH reduction without the aid of acids is limited to very electron-deficient C=C double bonds.

Interestingly, **1** is not reduced in acetonitrile (Table 2). The result may be rationalized based on the proposition by van Eikeren and Grier[22] that protic media greatly lower the free energy of activation for the dihydronicotinamide reduction of carbonyl compounds: in the present system, for example, solvent alcohol may provide a means of stabilizing the developing negative charge on the substrate β-carbon in the transition state through hydrogen bonding. However, **3** ($2\sigma^\circ_{\text{COOEt}}=0.60$), a less electron-deficient olefin is reduced in acetonitrile in 10% yield. Therefore, it is difficult to provide a consistent elucidation on the yield based on the proposition of van Eikeren and Grier.[22]

Here, it is worth mentioning that the disappearance rate of BzlNicH in the presence of **1** in acetonitrile is almost comparable with that in ethanol, despite the difference in the yield. Since the reduced product of **1** was not found in acetonitrile, the disappearance of BzlNicH should be attributed to the formation of some

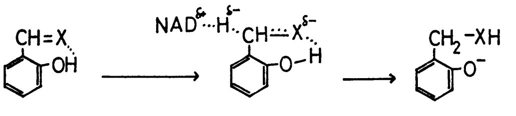
Table 2. Product analyses of the BzlNicH reduction[a] and the influence of $Mg(ClO_4)_2$ on NMR chemical shift of α-proton of substrates[b]

Substrate	Yield of reduced products (%)					NMR shift to lower field (Hz)
	CH_3CN			CH_3OH		
	None	$Mg(ClO_4)_2$[c]	CH_3COOH[c]	None	CH_3COOH[c]	
1	0	62±7		10±4	71(42)[d]	7
2	0	22±4	8±3	0	16±6	3
3	10±2	96±6				10
4	0	0				2
2OH				0	5±3	
2NO₂				5±2	15±5	

a) 2 h reflux in the dark. b) [substrate]=1.0 M, [$Mg(ClO_4)_2$]=1.4 M, solvent: CD_3CN. c) [substrate]=0.10 M, [BzlNicH]=0.12 M, [$Mg(ClO_4)_2$]=0.14 M, [CH_3COOH]=1.0 M. d) Isolated yield for the 2 h reaction at room temperature in the dark.

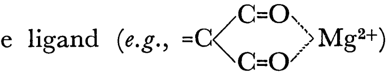
by-products.

2OH is a suitable substrate to evaluate the effectiveness of the ortho hydroxyl group in the reduction of C=C double bonds. The NMR coupling constant between two olefinic protons (16 Hz) is compatible with *trans*-configuration, so that the steric hindrance between ortho hydroxyl group and β-nitro group would be almost disregarded. Table 3 indicates that the relatively fast disappearance of BzlNicH occurs on the addition of **2OH**, but the corresponding reduced product was neither detected by NMR nor isolated by extraction with chloroform. It would appear, therefore, that the fast disappearance of BzlNicH should be ascribed to the decomposition catalyzed by the ortho hydroxyl group.[19] In fact, the NMR spectrum of the reaction mixture showed that 20—40% of **2OH** were left unreacted. These results endorse that the ortho hydroxyl group is not effective in the reduction of the C=C double bond of **2OH** (and probably C=C double bonds in general). The finding provides a striking contrast to a number of precedents that the ortho hydroxyl group plays a crucial role in the dihydronicotinamide reduction of double bonds attached to aromatic rings.[23—26] The role of the ortho hydroxyl group has been ambiguous due to two undistinguishable effects: that is, the ortho hydroxyl group can activate the carbonyl (and its analogs) in the initial state through hydrogen bonding and, at the same time, it can stabilize the developed negative charge in the transition state by means of specific solvation (or intramolecular general acid catalysis).[20,22,26)]



(3)

We consider that the contribution of the ortho hydroxyl group in the initial state is less significant in the reduction of C=C double bonds, because it is well-known that C=C double bonds (as π bases) very weakly interact with the phenolic hydroxyl group.[11] On the other hand, the stabilization of the developing carbanion by the hydroxyl group in the transition state is still probable. The claim is supported by an example of the intermolecular reaction that BzlNicH reduction of **2** is general acid catalyzed by added acetic acid (*vide post*). Thus, the ineffectiveness of the ortho hydroxyl group suggests that, in the reduction of C=X (X: hetero atom) double bonds, hydrogen bonding with the ortho hydroxyl group in the initial state plays an indispensable role for the subsequent hydrogen transfer.

Influence of Added Mg²⁺ Ion. Prior to kinetic and product analyses, the possible interaction between substrates (**1**—**4**) and $Mg(ClO_4)_2$ (1.4 equivalents of substrate) was dissected. The UV spectrum of these four substrates (0.1 mM) in dry acetonitrile was hardly affected by added Mg^{2+} ion. The IR absorption band based on $\nu_{C=O}$ of **3** and **4** (solvent, acetonitrile) did not change appreciably in the presence of Mg^{2+} ion. On the other hand, added Mg^{2+} ion caused a significant change in the NMR chemical shifts of α-protons of **1** and **3** to lower field (Table 2), while those of **2** and **4** scarcely shifted. It is implicated, therefore, that the metal-substrate interaction does exist in **1** and **3** at least at the concentration used for the NMR measurements (*ca.* 1.0 M). On the contrary, the interaction with **2** and **4** is almost disregaded. It is expected that **3** would bahave as a bidentate ligand (*e.g.*,  $=C\langle{}^{C=O}_{C=O}\rangle Mg^{2+}$), while the similar interaction between metal and **4** would be accompanied by condsiderable difficulty due to energetically-unfavorable conformational change (*e.g.*, chair form or other non-planar conformations between carbonyl and C=C double bond).

The reduction of **1**, **2**, and **3** was remarkably facilitated by added Mg^{2+} ion (Table 2). In particular, **3** was reduced quantitatively to the corresponding methylene compound within 2 h. It is interesting that the yield in the presence of Mg^{2+} ion shows a trend parallel to the NMR chemical shift. On the other hand, **4** which hardly interacts with Mg^{2+} ion was not subject to the Mg^{2+}-assisted reduction at all. Conceivably, the steric factor markedly suppresses the reactivity of **4**.

Ohno *et al.*[7,27] found that BzlNicH strongly interacts with Mg^{2+} ion. We also confirmed in the present study that the λ_{max} of BzlNicH in acetonitrile (345 nm) shifts to 352 nm on the addition of 2.0 equivalents of $Mg(ClO_4)_2$. The result substantiates, together with the absence of the spectral change of the substrates (*vide supra*), that BzlNicH preferentially interacts with Mg^{2+} ion. The parallel relation between the NMR shift and the yield suggests, however, that the interaction with the substrates is not necessarily meaningless: for example, the interaction could occur at least in the transition state. It is expected, of course, that, when the coordination ability of substrate is relatively superior,[6,28] the interaction with substrate occurs predominantly.

The kinetic measurements in the presence of Mg^{2+} ion were carried out at 30 °C in dry acetonitrile. Since **1** and **2** are not reduced by BzlNicH in the absence of Mg^{2+} ion, the decay of BzlNicH at $[Mg(ClO_4)_2]=0$ is attributed to the production of some by-products. The

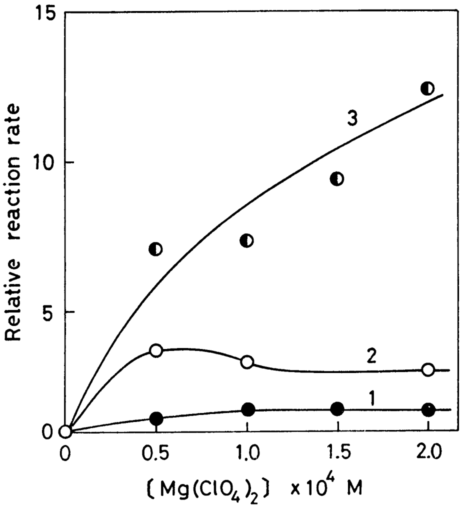
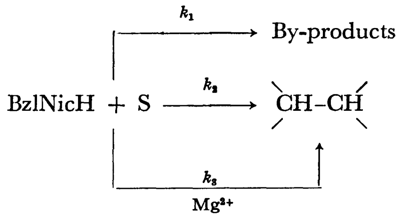


Fig. 1. $[Mg(ClO_4)_2]$ *vs.* relative reaction rate in acetonitrile.
$[BzlNicH]=1.00\times10^{-4}$ M, $[substrate]=5.00\times10^{-3}$ M.

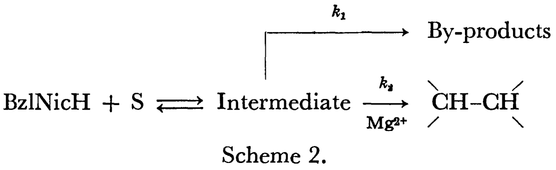
reaction rates were determined by varying the concentration of Mg^{2+} ion while maintaining the concentration of BzlNicH constant. The relative reaction rates thus obtained were plotted as a function of the concentration of Mg^{2+} ion in Fig. 1. A small rate augmentation of 1.4—3.3 fold was observed for the reaction with **1** and **2**, and the reaction with **3** was further enhanced (7—12 fold). The largest rate increase in **3** is consistent with the expectation that **3** interacts with Mg^{2+} ion most strongly among three substrates employed. The reaction rates showed saturation tendencies with increasing Mg^{2+} concentration, but the clear rate maximum which was reported for the reaction with 2-benzoylpyridine[6] was not found.

Scheme 1 may be proposed for the reduction of **3**, where the k_3 term involves the reaction of Mg^{2+}-coordinated BzlNicH and substrate ($k_{\mathrm{Mg}^{2+}-\mathrm{BzlNicH}}$) and the reaction of BzlNicH and Mg^{2+}-coordinated substrate ($k_{\mathrm{Mg}^{2+}-\mathrm{S}}$). If a relation, $k_2 < k_{\mathrm{BzlNicH}}, k_{\mathrm{Mg}^{2+}-\mathrm{S}}$, is assumed, the experimental results for **3** is explained consistently by Scheme 1.



Scheme 1.

The reaction with **1** and **2** may be also rationalized by Scheme 1, but a question arises whether or not the drastic change in the yield (Table 2) can be explained by such small rate augmentations (for example, only 1.7 fold for **1**). It seems as if scheme 2 is more plausible for the reaction with **1** and **2** which features the rate-limiting formation of an intermediate followed by a Mg^{2+} dependent partition.



Scheme 2.

According to Scheme 2, the discrepancy between the slight rate enhancement and the dramatic improvement of the yield can be readily explained. It becomes difficult, however, to rationalize the saturation phenomena, for Mg^{2+} ion is not involved in the rate-limiting step in Scheme 2. Thus, both Schemes may be concurrent in the reduction of **1** and **2**.

Influence of Added Acetic Acid. The role of metal ion in dihydronicotinamide reduction is complicated because of its potential interaction with dihydronicotinamide and substrate both in the initial and transition states. In contrast, the role of Bröted acid is fairly simplified, since the interaction with dihydronicotinamide is offset as acid-catalyzed decomposition by the blank reaction in the absence of substrate. In addition, the interaction with substrate in the initial state (*i.e.*, specific acid catalysis) is hardly conceivably. Thus, the interaction occurs only in the transition state.

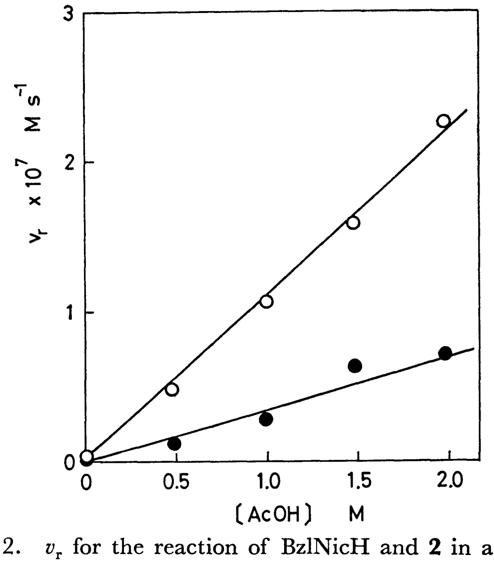


Fig. 2. v_r for the reaction of BzlNicH and **2** in acetonitrile (○) and in ethanol (●) plotted as a function of the concentration of acetic acid. [BzlNicH] $= 1.00 \times 10^{-4}$ M, [**2**] $= 5.00 \times 10^{-3}$ M.

As shown in Fig. 2, plots of v_r *vs.* [AcOH] gave good linear relations ($r > 0.98$), and Eq. 4 follows,

$$v_r = k_r[\mathrm{BzlNicH}][\mathrm{S}] + k_{\mathrm{AcOH}}[\mathrm{BzlNicH}][\mathrm{S}][\mathrm{AcOH}], \quad (4)$$

where k_{AcOH} is the third-order rate constant for acetic acid assisted rate acceleration which can be calculated from the slope in Fig. 2. The results are summarized in Table 3.

The reaction of BzlNicH and **2** is very slow without acetic acid, and the corresponding reduced product is not obtained. The addition of acetic acid brought forth the enhancement of the rate and the yield simultaneously. Evidently, acetic acid is involved in the rate-limiting step, and the role is reasonably designated as a general acid catalysis.[20,22] Thus, the reaction mechanism analogous to Scheme 1 is in effect for **2**.

The reduction of **1** is not the case, however. As shown in Tables 2 and 3, added acetic acid does not accelerate the disappearance of BzlNicH at all despite the fact that the yield is remarkably enhanced.[18] The discrepancy cannot be explained by Scheme 1 in which the improvement in the yield *must be* accompanied by the rate enhancement. Alternatively, Scheme 2 may be adopted as a possible mechanism for **1**. Although it is difficult to specify "intermediate" at present, the formation of some radical species is expected.[18,29,30]

Concluding Remark. The various kinds of electron-deficient C=C double bonds are reduced by the aid of metal ion or acetic acid, as has been reported by some groups.[18,31,32] However, the combination of kinetic studies with product analyses clarified that the role of added acids is not simple. We believe that the clear understanding of the behavior of metal ions and Brönsted acids would bear further application of nonenzymatic dihydronicotinamide reductions.

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