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Interaction of Metal Ions with NADH Model Compounds. Cupric Ion Oxidation of Dihydronicotinamides

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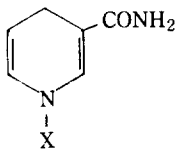
Kinetic studies on cupric ion (Cu^{2+}) oxidation of 1-benzyl- and 1-aryl-1,4-dihydronicotinamides (XNAH) in aqueous solution were performed. In the presence of dioxygen (O_2), the reaction followed first order kinetics with respect to both XNAH and Cu^{2+}. The oxidation reaction was found to be independent and parallel to the acid-catalyzed hydration reaction of XNAH. The catalytic role of Cu^{2+} for the oxidation of XNAH in the presence of O_2 was attributed to Cu^{2+}/Cu^{+} redox cycle by the reactions with XNAH and O_2. The second order rate constants of the Cu^{2+} oxidation reaction k_{Cu} and acid-catalyzed hydration reaction k_H were strongly dependent on the nature of the substituents in 1-aryl moiety. The slopes of log k_{Cu} vs log K_H and log k_{Cu} vs σ_p of the substituents plots were 1.64 and −2.2, respectively. This revealed the greater sensitivity of the oxidation reaction rate to the electron density on the ring nitrogen than the hydration reaction rate. A concerted two-electron transfer route involving XNAH-Cu^{2+} complex was proposed for mechanism of the oxidation reaction.

Introduction

The redox couple NADH/NAD^+ is one of the most important coenzymes in biological systems. In consequence the chemical reactions of NADH model compounds in enzyme-free systems have been a major interest to chemists.[1] The detailed mechanism of NADH model compounds reduction of organic substances is still in controversy whether the net transfer of hydride from the 4-position of the dihydropyridine ring to the oxidizing agent is a single step process or via multi-step e^-, H^+, e^- mechanism.[2] Meanwhile, it was shown that oxidation of NADH and its analogues by inorganic one-electron oxidants such as ferrocenium cation[3,4] and ferricyanide anion[5-7] proceeds by rate-determining initial one-electron transfer from dihydronicotinamide moiety to the oxidizing agent. The logarithm of the reaction rate constant appeared to vary linearly with E^O for ferrocenium/ferrocene couples.[4] Divalent metal ions exert large effects on reduction of organic compounds by dihydronicotinamides.[1b,1c] They catalyze the reaction and, sometimes, increase stereoselectivity in the reduction.

In this paper we report oxidation of 1-benzyl- and 1-aryl-substituted-1,4-dihydronicotinamides **1-6** by Cu^{2+} in aqueous media. The effect of the nature of the 1-substituents on the oxidation rate was evaluated and correlated with that on the hydration reaction of the dihydronicotinamides.[8] We also show a large effect of oxygen on the kinetics of the oxidation reaction.



1, X = $C_6H_5CH_2$ **2,** X = p-$CH_3OC_6H_4$
3, X = p-$CH_3C_6H_4$ **4,** X = C_6H_5
5, X = p-ClC_6H_4 **6,** X = p-CNC_6H_4

Experimental

Materials. The NADH model compounds 1-benzyl-1,4-dihydronicotinamide(**1**), 1-(p-methoxyphenyl)-1,4-dihydronicotinamide(**2**), 1-(p-methylphenyl)-1,4-dihydronicotinamide(**3**), 1-phenyl-1,4-dihydronicotinamide(**4**), 1-(p-chlorophenyl)-1,4-dihydronicotinamide(**5**) and 1-(p-cyanophenyl)-1,4-dihydronicotinamide(**6**) were available from an earlier study.[8] Vacuum dried $CuCl_2$(Junsei) was used as a source of Cu^{2+}. Deionized glass-distilled water was used. All other chemicals were readily available from commercial sources.

Kinetic Studies. Rate constants for the disappearance of dihydronicotinamides (XNAH) **1-6** were determined at 25 °C with a Spectronic 21 or Beckman DU 8B UV-VIS spectrophotometer with a thermostatted cell holder. The ionic strength of solutions was held constant at 0.1 M by the addition of NaCl. The buffer system was 0.01 M cacodylate. The reaction was made by mixing a solution of XNAH in ethanol with an aqueous Cu^{2+} solution at a desired pH (or H^+ concentration) in a quartz mixing cell. The final solvent composition was 5% EtOH-95% H_2O and the concentration of XNAH was 1.0×10^{-4} M.

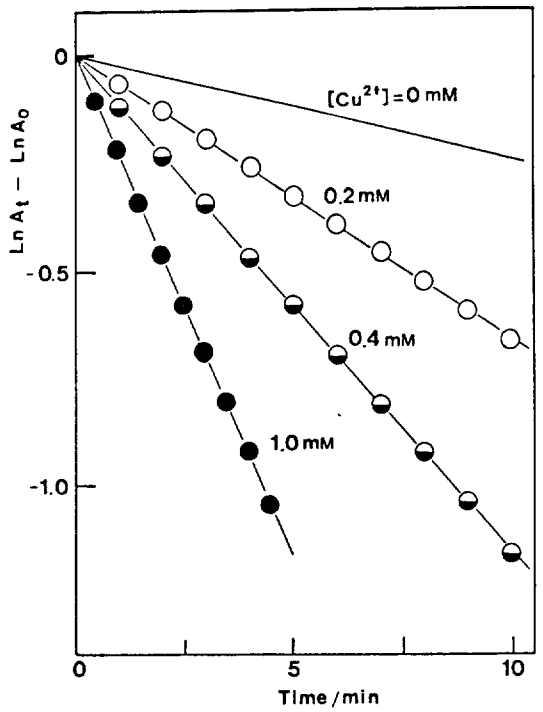


Figure 1. Plots of logarithm of absorbance of BNAH at 354 nm against reaction time according to eq. 1 at various concentrations of Cu^{2+} shown. The pH of solutions was 5.3.

To investigate an effect of oxygen, the anaerobic kinetic runs were carried out. For removal of oxygen from solutions, nitrogen gas which was purified by passing through NH_4VO_3/Zn(Hg) was bubbled into a desired reaction mixture without XNAH in a quartz cell with a stopcock for an hour and then 0.01 m*l* of 0.01 M solution of XNAH in ethanol was added through a Hamilton syringe. The stopcock was immediately closed, the solution was mixed and the reaction was followed spectrophotometrically.

Disappearance of XNAH was followed by observing the decrease in absorbance (A) of the solution during the reaction at their characteristic absorption peaks, 340-360 nm region. For dihydronicotinamides **1, 3** and **5,** of which reaction products do not show appreciable absorption at the measuring wavelength, the pseudo first order rate constant (k_ψ) were determined from plots according to equation 1.

$$\ln A_t - \ln A_o = -k_\psi t \quad (1)$$

For compounds **2, 4** and **6** whose reaction products have some absorption at the measuring wavelength, k_ψ's were determined from the plots of $ln\ (A_t - A_{t+\Delta t})$ against time:[9]

$$\ln (A_t - A_{t+\Delta t}) = -k_\psi t + \ln (1 - e^{-k\psi \Delta t}) + \text{constant} \quad (2)$$

Results and Discussion

Evidences of Oxidation and the Rate Constants. Figure 1 shows plots of the logarithm of absorbance of 1-benzyl-1,4-dihydronicotinamide (BNAH) **1** at 354 nm against time (eq 1) at various concentration of Cu^{2+}. The Figure shows a good linearity, which indicates that the disappearance of BNAH follows pseudo first-order kinetics both in the presence and in the absence of Cu^{2+}. It also shows the linear increase of the slope k_ψ, the pseudo first-order rate constant, with [Cu^{2+}]. Such relationships were also obtained with other XNAH's studied here.

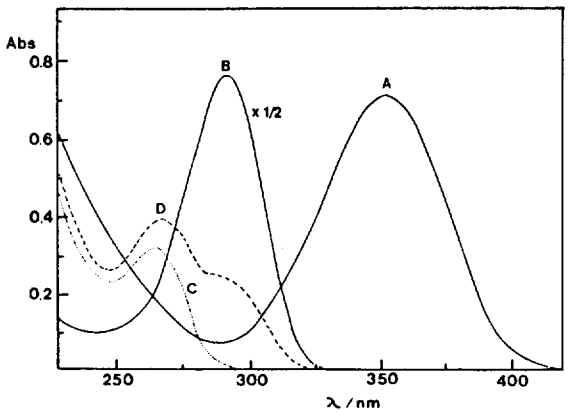


Figure 2. UV spectra of BNAH (A), BNAH without Cu^{2+} after one day (B), BNAH with Cu^{2+} after one day (D) and 1-benzyl-3-carbamoylpyridinium salt (C). For details on conditions, see text.

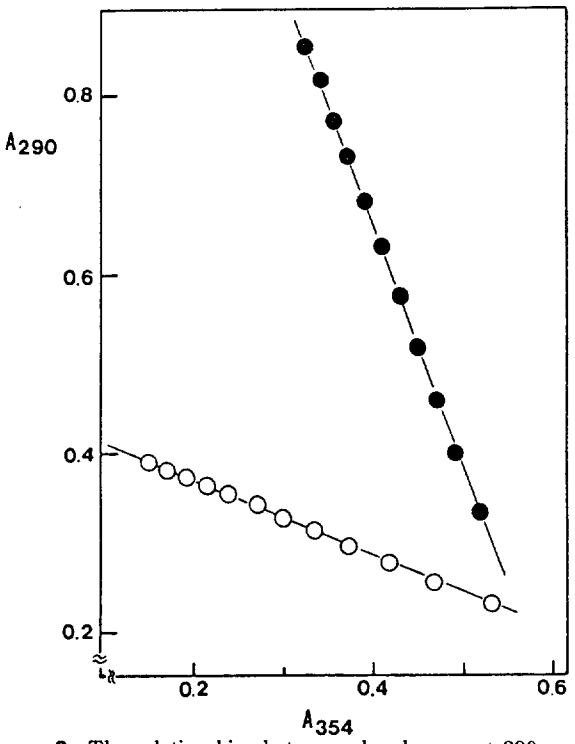


Figure 3. The relationships between absorbances at 290 nm and 354 nm of 1.0×10^{-4} M BNAH solutions in the absence of Cu^{2+} (●) and in the presence of 2.0×10^{-4} M Cu^{2+} (○) at various reaction times. The pH of solutions was 6.0.

Dihydronicotinamides undergo H^+ catalyzed hydration reactions.[8] The enhanced rate of disappearance of XNAH in the presence of Cu^{2+} can be attributed either to a catalytic effect of the metal ion on the hydration or to other parallel reaction in which Cu^{2+} is involved. To clarify this, the UV spectra of the reaction products from BNAH were taken and shown in Figure 2. The A and C represent spectra of BNAH itself and its oxidized product, 1-benzyl-3-carbamoylpyridinium salt, respectively. The spectra B and D were taken after standing BNAH solution in pH 5.9 buffer for a day without Cu^{2+} (B) and with 5.0×10^{-4} M Cu^{2+} (D). B represents the spectrum of the hydrated product of BNAH, 1-benzyl-6-hydroxy-1,4,5,6-tetrahydronicotinamide.[10] Com-

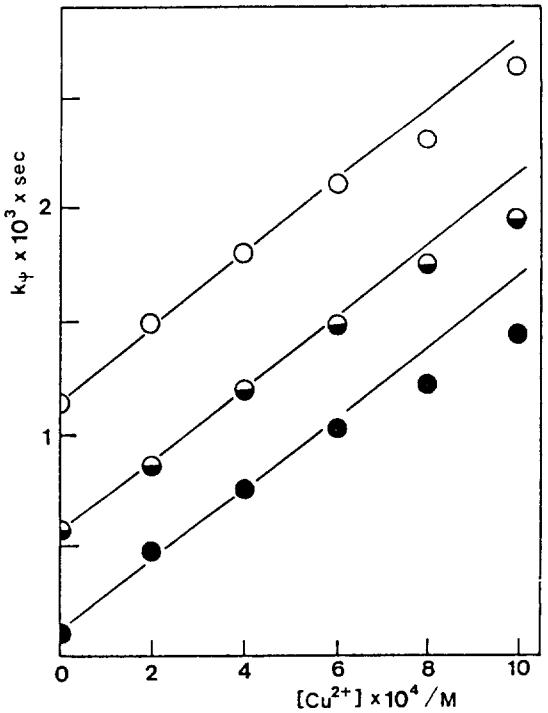


Figure 4. The plots of the pseudo first-order rate constant k_ψ of 1-(p-methylphenyl)-1,4-dihydronicotinamide **3** as functions of $[Cu^{2+}]$. The concentrations of H^+ in solutions are 1.0×10^{-3} (○), 5.0×10^{-4} (◒) and 1.0×10^{-4} M (●).

paring the spectrum D with the spectra B and C, it is clear that BNAH undergoes both hydration and oxidation reactions in the presence of Cu^{2+}: addition of Cu^{2+} to XNAH solutions causes an additional reaction, oxidation of XNAH.

Now the question is whether the cupric ion causes just oxidation of XNAH or it also has any effect on the hydration reaction. Since the hydrated product has the characteristic absorption band at 290 nm, and both BNAH itself and its oxidized product do not have any appreciable absorption at the wavelength, the absorbance at 290 nm reflects only hydration reaction product. Figure 3 shows the relationships between absorbance values at 290 nm and 354 nm for 1.0×10^{-4} M BNAH solutions in the absence and in the presence of 0.2 mM Cu^{2+} at pH 6.0 taken at various reaction times. Good linearity between the absorbances values was observed, but the slopes were different. When the cupric ion was absent, the slope was -2.67: the minus sign reflects that the hydrated product absorbing at 290 nm is formed at the expense of BNAH absorbing at 354 nm, and the value 2.67 is the ratio of the molar absorptivities of the hydrated product and BNAH itself. In the presence of 0.2 mM Cu^{2+}, the slope was decreased to -0.43. This suggests that only 1/6 of the BNAH consumed undergoes hydration reaction and the remaining 5/6 is oxidized. Using the same experimental data, the pseudo first-order rate constants (k_ψ's) for the disappearance of BNAH were calculated to be 1.56×10^{-4} sec^{-1} in the absence of Cu^{2+} and 9.44×10^{-4} sec^{-1} in the presence of 0.2 mM Cu^{2+}. The ratio is also 1:6. Therefore the six times increase in the rate constant for the disappearance of BNAH in the presence of 0.2 mM Cu^{2+} can be attributed solely to the oxidation of BNAH by Cu^{2+}. Thus we can conclude that the presence of Cu^{2+} has no noticeable effect on the hydration reaction of BNAH in our experimental condition.

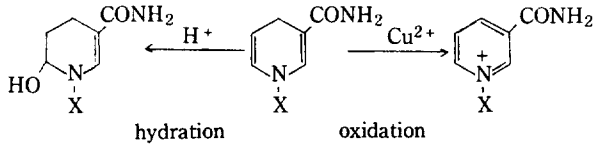
Table 1. Second Order Rate Constants of Hydration k_H and Cupric Ion Oxidation k_{Cu} of Dihydronicotinamides at 25°C in 5% Ethanol-95% H_2O of Ionic Strength 0.1 M

Compounds	x	k_H, $M^{-1}sec^{-1}$	k_{Cu}, $M^{-1}sec^{-1}$
1	$C_6H_5CH_2$	13.6	3.97
2	$CH_3OC_6H_4$	1.37	2.35
3	$CH_3C_6H_4$	1.14	1.55
4	C_6H_5	0.665	0.524
5	ClC_6H_4	0.352	0.195
6	CNC_6H_4	0.030	0.004

At a given pH or H^+ concentration, the pseudo first-order rate constant k_ψ for the disappearance of XNAH was varied linearly with $[Cu^{2+}]$, except slight negative deviation at high $[Cu^{2+}]$. This relationship was shown for 1-(p-methylphenyl)-1,4-dihydronicotinamide **3** at various HCl concentration in Figure 4. It is evident from this Figure that the second-order rate constant for the oxidation of XNAH by Cu^{2+}, k_{Cu}, which is the slope of the k_ψ vs $[Cu^{2+}]$ plot, is independent of $[H^+]$. The intercept, k_ψ at $[Cu^{2+}] = 0$, was shown to be proportional to $[H^+]$ and the proportionality constant, k_H, is the second-order rate constant of the hydration reaction of XNAH catalyzed by H^+.[8] From Figure 4 and our discussion in the preceding paragraph, it is evident that the pseudo first-order rate constant for the disappearance of XNAH can be written in terms of two independent parallel reactions.

$$k_\psi = k_H[H^+] + k_{cu}[Cu^{2+}] \quad (3)$$

Also, the reactions can be written in the following Scheme:



From the intercept and the slope of the plots of k_ψ vs $[Cu^{2+}]$ as shown in Figure 4, the second order rate constants, k_H and k_{Cu} were obtained and the results are summarized in Table 1.

Effect of Dioxygen-Catalytic Role of Cu^{2+} in the Presence of O_2. The fact that the oxidation of XNAH by Cu^{2+} is first-order with respect to the initial concentration of Cu^{2+} suggests that the concentration of the oxidizing agent remains constant during the reaction. This would be no wonder if $[Cu^{2+}] \gg [XNAH]$. However, when $[Cu^{2+}]$ is not so high compared to [XNAH] as in the cases shown in Figures 1 and 4, there should be a route for regeneration of Cu^{2+} to maintain the concentration constant. Since we did not add any other oxidizing agent to reoxidize the reduced copper purposely, it seems natural to assume that the Cu^{2+} is regenerated by dissolved O_2 in the reaction system. In fact, it is known that molecular oxygen can be utilized as an oxidant in Cu^{2+}-catalyzed oxidation reactions by participation in Cu^{2+}/Cu^+ redox cycle.[11,12] The concentration of dissolved O_2 in aqueous solution at 25 °C is calculated to be 0.25 mM.[13] This amount is sufficient to regenerate Cu^{2+} from its reduced form produced as a result of oxidation of 1.0×10^{-4} M XNAH.

Figure 5 shows the results of the aerobic and the anaerobic kinetic runs: A is the result obtained in an air-saturated solution without Cu^{2+}; B and C are the data taken in

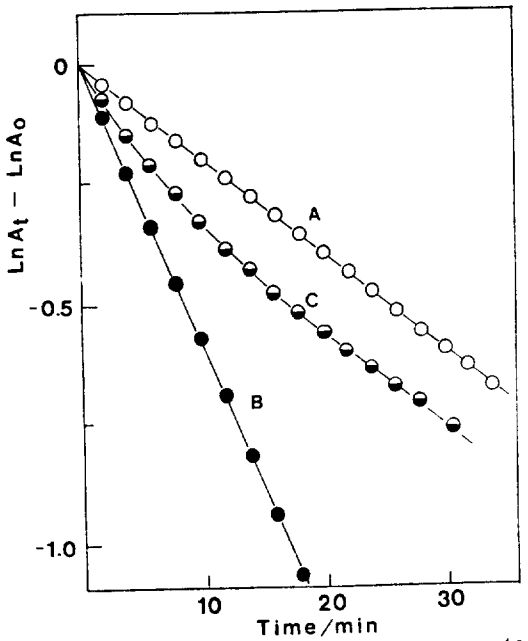


Figure 5. Plots of logarithm of absorbance of 1.0×10^{-4} M BNAH solutions at 354 nm against reaction time according to eq 1. A is the result taken in an air saturated solution without Cu^{2+}. B and C represent data from air saturated and N_2 purged solutions, respectively, containing 1.0×10^{-4} M Cu^{2+}. The pH of solutions was adjusted to 5.9, and the final solvent composition was 1% aqueous ethanol.

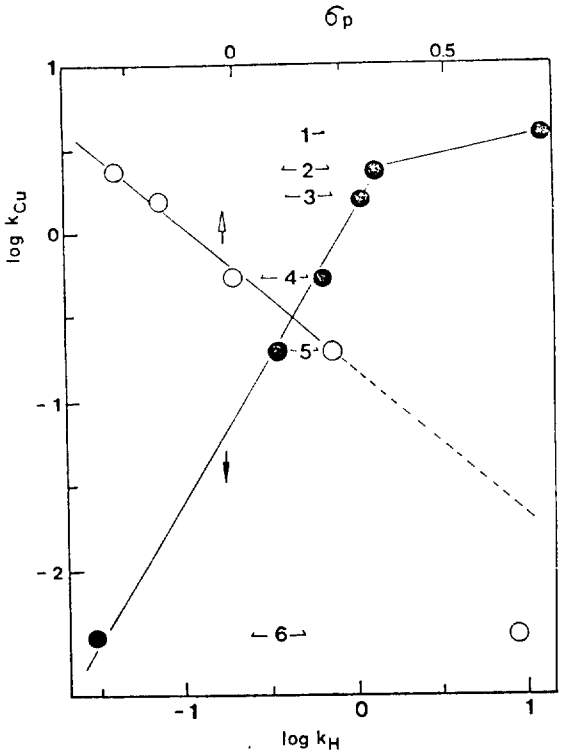
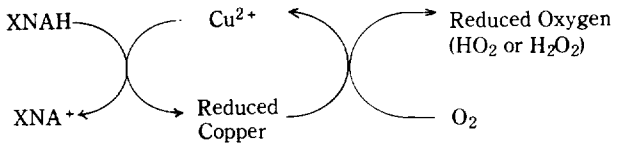


Figure 6. Hammett type plots of the second order Cu^{2+} oxidation rate constants of dihydronicotinamides against hydration rate constants (●) and σ_P of substituents in 1-aryl moiety (○).

air-saturated and deaerated solutions with 1.0×10^{-4} M Cu^{2+}, respectively. In contrast to the excellent linearity observed in A and B, C deviates considerably from the pseudo first-order rate equation. The tangent of plot C, which is the apparent rate constant k_ψ, is close to the slope of B at the initial stage of the reaction. But it approaches to that of A as the reaction proceeds. The diminution of Cu^{2+} with the progress of the reaction can accounts for this behavior, since Cu^{2+} cannot be regenerated in the absence of oxygen. Alternatively, this result can be regarded as an evidence that Cu^{2+} plays a catalytic role on the oxidation of XNAH in the presence of dioxygen. The overall reaction can be expressed in the following cyclic Scheme:



Effect of Substituents on Oxidation Rate and Reaction Mechanism. The data in Table 1 show strong dependence of both k_H and k_{Cu} on the nature of the substituent in 1-aryl moiety of XNAH. Figure 6 presents the plots of log k_{Cu} against log k_H and σ_P constants of the substituents in 1-aryl groups. The good linear relationships between these values are evident. The Hammett relationship between k_{cu} and k_H can be expressed as eq 4 except X = CNC_6H_4.

$$\log k_{cu} = 1.64 \log k_H + 0.079 \quad (r = 0.999) \qquad (4)$$

Also, the correlation between log k_{Cu} and σ_P obeyed the following form except X = $C_6H_4CH_2$.

$$\log k_{cu} = -2.2\sigma_p - 0.22 \quad (r = 0.996) \qquad (5)$$

It is obvious from these results that the Cu^{2+} oxidation rate is more sensitive to the electron density on the ring nitrogen than the hydration reaction rate.

The Cu^{2+} oxidation rate constants k_{Cu} obtained in this investigation are 2-4 times greater than the ferricyanide oxidation rate constants for the same XNAH's.[7] This is quite unusual in view of the kinetic-thermodynamic correlation when one considers the difference in the standard redox potentials E^0 of Cu^{2+}/Cu^+ 0.153 V and $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$ 0.45 V.[14] One of the possible explanations for this is hydride transfer mechanism for cupric ion oxidation, while the ferricyanide oxidation involves the rate determining electron transfer step.[7] However, this is unlikely in the light of hydride chemistry.

An alternative explanation is involvement of complexation between XNAH and Cu^{2+}. This could reduce the energy barrier for rate determining electron transfer step and accelerate the reaction. The complex formation between XNAH and metal ions accounted for the catalytic effect of the ions in XNAH reduction of organic compounds in organic media.[15,16] The formation of reactive complex was also reported in ferric ion oxidation of NADH.[17,18] We attempted to obtain an evidence of the XNAH-Cu^{2+} complex formation, but failed presumably due to small complex formation constant (*vide infra*). The first-order kinetics for the disappearance of XNAH in both XNAH and Cu^{2+} implies that only very small fractions of XNAH and Cu^{2+} are complexed, if any, in our experimental condition. Moreover the independence of k_H on [Cu^{2+}] supports this view: The hydration reaction of XNAH involves rate determining protonation step, and the step is expected to be inhibited by XNAH-Cu^{2+} complex formation due to electrostatic effect. This argument was

supported from studies on the effect of metal ions on the hydration reaction in non-aqueous media.[19] The apparent first-order rate constant k_ψ is expected to decrease as the fraction of the complexed XNAH increases at higher concentration of Cu^{2+}.[20] The negative deviation from linearity in k_ψ vs $[Cu^{2+}]$ plots at high concentration of Cu^{2+} (Figure 4) seems to reveal this. Thus the deviation can be taken as an evidence of weak XNAH-Cu^{2+} complexation.[21]

It is of interest to note that O_2 enhances the Cu^{2+} oxidation rate (possibly by oxidation of reduced copper to Cu^{2+}), whereas it inhibits the ferricyanide oxidation of XNAH.[7] The latter observation was attributed to the regeneration of XNAH from $XNAH^+$ by reaction with O_2^- which is formed from the reaction between XNA and O_2. The $XNAH^+$ and XNA are reaction intermediates and are formed by initial one-electron transfer and following not-rate determining steps.

$$\mathrm{XNAH} \underset{O_2}{\overset{-1e}{\rightleftharpoons}} \mathrm{XNAH^+} \xrightarrow{-H^+} \mathrm{XNA} \underset{O_2}{\overset{-1e}{\rightleftharpoons}} \mathrm{XNA^+} \quad (6)$$

The oxidation of XNAH to XNA^+ is an overall two-electron process. Also Cu^{2+} can be reduced by two electrons to Cu as well as by one electron to Cu^+. Therefore the Cu^{2+} oxidation of XNAH can proceed via one-electron transfer reaction as shown in eq 7 (a concerted or consecutive process) or via a two electron route in eq 8: The former requires two Cu^{2+} per one molecule of XNAH, while the latter mechanism involves only one Cu^{2+}.

$$\mathrm{XNAH + 2Cu^{2+} \longrightarrow XNA^+ + 2Cu^+ + H^+} \quad (7)$$

$$\mathrm{XNAH + Cu^{2+} \longrightarrow XNA^+ + Cu + H^+} \quad (8)$$

In the first mechanism, the possibility of a concerted process can be ruled out since the reaction was observed to be first order in Cu^{2+}. The consecutive two one-electron process in the first mechanism which is similar to the mechanism of ferricyanide oxidation of XNAH,[7] is less likely as we could not observe the inhibitory effect of O_2 expected from reaction 6. The second mechanism eq 8 does not contradict with our experimental findings. However this mechanism does not necessarily imply one step two-electron transfer from XNAH to Cu^{2+}. It only suggests that the transfer of the second electron to Cu^+ is very fast and completed before break-off of $XNAH^+$-Cu^+.

$$\mathrm{XNAH + Cu^{2+} \rightleftharpoons \{XNAH - Cu^{2+}\} \xrightarrow[slow]{} \{XNAH^+ - Cu^+\}}$$
$$\mathrm{\xrightarrow[fast]{} \{XNAH^{2+} - Cu\} \longrightarrow XNA^+ + Cu + H^+} \quad (9)$$

The resultant Cu might undergo auto redox reaction with Cu^{2+} to produce Cu^+ which is oxidized to Cu^{2+} by O_2. The superoxide O_2^- would react with H^+ to form HO_2 and H_2O_2 by further reactions.

Conclusions

We have demonstrated that XNAH is oxidized by Cu^{2+} in aqueous solution. The reaction is first order with respect to both XNAH and Cu^{2+}. The oxidation reaction is independent and parallel to the acid-catalyzed hydration reaction of XNAH. The oxidation and hydration reaction rates depend strongly on the electron-withdrawing characteristics of substituents in 1-aryl moiety. The Hammett type plots of log k_{Cu} against log k_H and σ_p yielded good linearity with slopes 1.64 and −2.2, respectively. This indicates greater sensitivity of the Cu^{2+} oxidation reaction rate of XNAH to the electron density on the ring nitrogen and reveals electron transfer process in the rate determining step of the oxidation reaction. In the presence of dioxygen, Cu^{2+} behaves as a catalyst for the oxidation of XNAH. Though the detailed mechanism for the oxidation is not fully elucidated at this point, a concerted two-electron transfer mechanism involving XNAH-Cu^{2+} complex was found to be consistent with our experimental observations.

Acknowledgement. This work was supported by the Basic Science Research Institute Program of Ministry of Education of the Republicl of Korea, 1987.

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13. The Henry's law constant of O_2 in water at 25 °C is 4.4 × 10^9 Pa. This gives the concentration of the dissolved O_2 under atmospheric pressure of P_{O_2} of 2 × 10^4 Pa (0.2 atm) as 0.25 mM.
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19. To be published.
20. The oxidation rate is given by:
Rate $= k[XNAH\text{-}Cu^{2+}]$
$= kK(1-f_{XNAH})(1-f_{XNAH}[XNAH]_t/[Cu^{2+}]_t) \times [XNAH]_t [Cu^{2+}]_t$
$= k_{Cu}[XNAH]_t [Cu^{2+}]_t$
Thus the apparent second order oxidation rate constant k_{Cu} decreases as the complexed fraction of XNAH, f_{XNAH} increases for a given complex formation constant K. The k is the intrinsic electron transfer rate constant of the complex and k_{Cu} becomes kK as $f_{XNAH} \rightarrow 0$.
21. At condition of $[Cu^{2+}] \gg [XNAH]$, the concentration of XNAH-Cu^{2+} complex is proportional to total concentration of XNAH by $[XNAH\text{-}Cu^{2+}] = K[Cu^{2+}][XNAH]_t/(1 + K[Cu^{2+}])$. Thus the first order kinetics in XNAH expressed in eq. 1 is still valid.

Four Crystal Structures of Dehydrated Ag^+ and Tl^+ Exchanged Zeolite A, $Ag_{12-x}Tl_x$-A, x = 2,3,4, and 5

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Four crystal structures of dehydrated Ag(I) and Tl(I) exchanged zeolite A, $Ag_{12-x}Tl_x$-A, x = 2,3,4, and 5, have been determined by single-crystal x-ray diffraction techniques. Their structures were solved and refined in the cubic space group *Pm3m* at 21(1) °C. All crystals were ion exchanged in flowing streams of mixed $AgNO_3$ and $TlNO_3$ aqueous solution, followed by dehydration at 350 °C and 2×10^{-6} Torr for 2 days. In all of these structures, one-sixth of the sodalite units contain octahedral hexasilver clusters at their centers and eight Ag^+ ions are found on threefold axes, each nearly at the center of a 6-oxygen ring. The hexasilver cluster is stabilized by coordination to eight Ag^+ ions. The Ag-Ag distance in the cluster, ca. 2.92Å, is near the 2.89 Å bond length in silver metal. The remaining five-sixths of the sodalite units are empty of silver species. The first three Tl^+ ions per unit cell preferentially associate with 8-oxygen rings, and additional Tl^+ ions, if present, are found on threefold axes in the large cavity.

Introduction

The properties of zeolites are sensitive to their cationic contents. A knowledge of the siting of these cations within a zeolite framework can provide a structural basis for understanding these properties. Thus far, the structures of Ag^+ [1,2], K^+ [3,4], Rb^+ [5], Cs^+ [6], Tl^+ [7], Mn(II) [8,9], Co(II) [9-12], Ni(II) [9], Zn(II) [9,13], Ca^{2+} [14], and Eu(II) [15] exchanged zeolite A[16] have been determined crystallographically.

Recently several crystal structures of fully Ag^+-exchanged zeolite A were determined.[17] Fully dehydrated Ag_{12}-A contains silver atoms, probably as hexasilver molecules centered within some of its sodalite cavities. Hexasilver is stabilized by coordination to eight Ag^+ ions very near the centers of the 6-oxygen rings on threefold axes.[2,17] Hermerschmidt and Haul identified Ag_6^{n+} (n<6) clusters in the sodalite cavity of dehydrated Ag^+-exchanged zeolite A using epr spectroscopy.[18] Their results were verified by Grobet and Schoonheydt[19] and reverified by the careful work of Morton and Preston who did epr measurements on isotropically pure samples of Ag_{12}-A[20].

The present study has been initiated to investigate the cation positions in the crystal structures of variously Ag^+ and Tl^+ exchanged zeolite A. It would be interesting to learn how different numbers of exchanged Tl^+ ions arrange themselves in the zeolite framework. Furthermore, because of the high scattering powers of Tl^+ and Ag^+, precise and reliable crystallographic determinations should be easy to achieve. The present work is preliminary to later studies of the crystal structure of $Ag_{12-x}Tl_x$-A treated with H_2 or other guest molecules.

Table 1. A Summary of Experimental Results

Crystal	Zeolite Cation Composition	Ion Exchange Mole ratio ($AgNO_3$:$TlNO_3$)	Ion Exchange Period	Dehydration Temp. (°C)	Dehydration Period (days)	Dehydration Pressure (Torr.)	Unit Cell Constant(Å)	Number of[a] Observed Reflections	R_1	R_2
1	$Ag_{10}Tl_2$-A	5:1	2 days	350	2	2×10^{-6}	12.300(2)[b]	302	0.054	0.057
2	Ag_9Tl_3-A	1.9:1	2 days	350	2	2×10^{-6}	12.243(2)	256	0.070	0.070
3	Ag_8Tl_4-A	1:1	2 days	350	2	2×10^{-6}	12.281(1)	377	0.067	0.067
4	Ag_7Tl_5-A	1:5	2 days	350	2	2×10^{-6}	12.263(1)	323	0.055	0.063

[a]Only those reflections for which $I > 3\sigma(I)$ were considered observed. [b]The number in parentheses is the esd in the units of the least significant digit given.