electrode. Their reduction is a two-step process and the corresponding $E_{1/2}$ values in DMF are given in Table II.

III. Electrochemical Reduction of BrAntr According to Method B. The compound was directly reduced at −1.55 ± 0.1 V. No redox catalyst was added because the Antr$^{\bullet}$ radicals were released for from the electrode where the side reaction (10) did not take place, as shown by kinetic data provided by Savéant et al.[16c] ($k_1 = 1.5 \times 10^5\ s^{-1}$). The selectivity for dichalcogenide over monochalcogenide was lost (entry 8) since the crude product contained anthracene (23%), the diselenide **1e**, and monoselenide **2e**[20] in similar amounts,[21] as well as a trace of triselenide derivative. Furthermore, the purification of the mono- and ditelluride by column chromatography was troublesome and the diselenide **1e** remained contaminated by some triselenide.[22] Fortunately the selectivity vis-a-vis **2e** could be restored since the cathodic reduction of **2e** is a four-step process whose first reduction step releases AntrSe$^-$ as shown in Scheme III, which is in agreement with the given $E_{1/2}$ values of Table II. Hence, the further reduction in situ of **2e** at −1.75 V (plateau of wave I) allowed the synthesis of **1e** in 54% yield, together with the corresponding triselenide in 6% yield, the synthesis of which probably resulted from the concomitant anodic oxidation of AntrSe$^-$ and Se_2^{2-}.

Conclusion

Method B will be more widely applicable than method A, which is restricted to aryl halides cathodically reducible at potentials close to those of Se and Te. However the synthesis of ditelluride derivatives requires method A, due to the instability of the Te_2^{2-} anions. Since we were able to prepare **1c–e** in useful yields in MeCN, we can anticipate that many diaryl dichalcogenides will be prepared in high yields by the electrochemical technique, since both 2-quinolyl[12c] and 9-anthryl[12j] radicals belong to the limited category of aryl radicals moderately reactive toward nucleophilic attacks. This technique will be particularly suitable for aryl radicals Ar$^{\bullet}$ substituted by unsaturated withdrawing groups such as nitrile or carbonyl functions. Indeed, their reactivity toward E_2^{2-} anions is expected to increase, as in the case where PhE$^-$ anions are used as nucleophiles,[12j] whereas their synthesis by classical means (lithiation and Se or Te insertion) cannot be carried out. Finally, it is worth noting that the synthesis of **1c** proceeded selectively in 70% yield at room temperature whereas its recent synthesis by S_NAr reaction under drastic conditions of temperature whereas its recent synthesis by S_NAr reaction under drastic conditions of temperature led to a mixture of **1c** and **2c** in 57% and 23% yields.[2a]

Experimental Section

Instrumentation and electrochemical cell have been described previously.[12h]

Bis(2-quinolyl) ditelluride (1d): orange crystals; mp 143–144 °C (acetone/hexane); ^1H NMR δ 7.47–7.53 (m, 2 H), 7.67–7.84 (m, 6 H), 8.02 (d, 2 H, J = 8.5 Hz), 8.20 (d, 2 H, J = 8.5 Hz); MS 512 (2, M$^+$), 128 (100, quinolyl$^+$). Anal. Calcd for $C_{18}H_{12}N_2Te_2$: C, 42.25; H, 2.35; N, 5.48; Te, 49.92. Found: C, 42.88; H, 2.54; N, 5.99; Te 49.36.

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Supplementary Material Available: Experimental details of methods A and B (4 pages). Ordering information is given on any current masthead page.

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[20] This compound was isolated in 31% yield from BrAntr and Na_2Se in DMF (Sandman, D. J. U.S. Patent 4,597,914, 1986).

[21] At the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium, Birmingham, U.K., July 25–29, 1983, D. J. Sandman et al. reported that BrAntr reacted with Na_2Se_2 in DMF to give **1e** and **2e** in yields of 28% and 21%, respectively.

[22] An elemental analysis of the orange powder indicated that it was roughly a mixture of **1e** (90%) and $AntrSe_3Antr$ (10%). This result was confirmed by MS and ^1H NMR.

Selective Aerobic Oxidative Dehydrogenation of Alcohols and Amines Catalyzed by a Supported Molybdenum–Vanadium Heteropolyanion Salt $Na_5PMo_2V_2O_{40}$

Ronny Neumann* and Michal Levin

Casali Institute of Applied Chemistry, Graduate School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, Israel 91904

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Introduction

In recent years there has been a renaissance in the investigation of the chemistry of heteropolyoxometallates[1] with an emphasis on their use as Bronsted acids[2] and oxidation catalysts.[3] An attractive and important aspect of these compounds is their inherent stability toward decomposition under strong oxidizing conditions. In oxidations most catalytic applications utilize the versatility of the Keggin-type heteropolyanions as they may contain a large variety of heteroatoms and are easily transferred into organic phases by lipoophilic cations or complexing agents. The oxidative catalytic activity of heteropolyoxometallates may be divided into four eneral reaction types: first, photoactivation of the catalyst, which in the excited state may catalyze dehydrogenations of alkenes and alkanes;[4] second, use of hydrogen peroxide as oxidant and complete molybdenum or tungsten Keggin compounds as catalyst precursors[5] in oxidations of alcohols, allyl alcohols, alkenes, and alkanes typical of such metal centers;[6] third, catalytic

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reactions where a lacunary or unsaturated Keggin heteropolyanion, $XM_{11}O_{39}^{q-}$, serves as an inorganic ligand for a transition-metal cation yielding a transition-metal-substituted heteropolyoxometallate, $XM'(L)M_{11}O_{39}^{q-}$, where X is the heteroatom, M is Mo or W, and M′ is a transition metal such as Co, Mn, Ru, etc. Reactions occurring at the substituted transition-metal center utilizing a variety of oxidants and transition metals have been observed.[7]

The fourth and final type of liquid-phase oxidation reactions found for heteropolyoxometallates are electron-transfer redox-type oxidations or dehydrogenations utilizing molybdenum–vanadium mixed-addenda Keggin anions $PMo_{12-x}V_xO_{40}^{(3+x)-}$ where $x \geq 2$ as catalysts. Such reactions are thought to proceed by the following generalized mechanism, eq 1.

$$\text{substrate} + PMo_{10}V^{V}_2O_{40}^{5-} \xrightarrow{-2H^+;\ -2e^-} \text{product} + H_2PMo_{10}V^{IV}_2O_{40}^{5-} \quad (1)$$

$$H_2PMo_{10}V^{IV}_2O_{40}^{5-} + \tfrac{1}{2}O_2 \rightarrow PMo_{10}V^{V}_2O_{40}^{5-} + H_2O$$

These catalysts (usually the most stable $PMo_{10}V_2O_{40}^{5-}$) are especially suited for this type of reaction because they combine the necessary oxidation potential required for substrate oxidation along with the ability to be reoxidized by molecular oxygen at reasonable rates. Substrates may be organic molecules as in the oxidation of sulfides,[8] dehydroogenation of dienes,[9] and the oxidative cleavage of ketones.[10] Additionally, substrates may be of an inorganic nature as in the oxidation of hydrogen bromide to molecular bromine[11] or primary catalysts such as Pd(0) where the product is Pd(II) as in Wacker-type oxidations.[12]

The research reported here describes the use of the mixed-addenda heteropolyanion salt $Na_5PV_2Mo_{10}O_{40}$ impregnated on activated carbon (PVMo/C) as a supported catalyst for carrying out new oxidative dehydrogenation reactions. In the past, $PV_2Mo_{10}O_{40}^{5-}$ has only been used as a catalyst in liquid-phase reactions in its acidic form, $H_5PV_2Mo_{10}O_{40}$, either in aqueous phases[8,10,12] or in organic phases by extraction of $H_5PV_2Mo_{10}O_{40}$ with tetraglyme as a complexing agent.[9,11] In addition to permiting reactions at a *neutral* pH the use of the supported catalyst naturally simplifies the catalyst recycle. The specific transformations performed are the novel selective dehydrogenations (by heteropolyanions) of benzylic and secondary alcohols to benzaldehydes and ketones, respectively, *without* overoxidation of the benzaldehydes to the carboxylic acids, eq 2. In a similar reaction benzylic amines are also

$$ArCH_2OH + PMo_{10}V^{V}_2O_{40}^{5-} \xrightarrow{-2H^+;\ -2e^-} ArCHO + H_2PMo_{10}V^{IV}_2O_{40}^{5-} \quad (2)$$

$$H_2PMo_{10}V^{IV}_2O_{40}^{5-} + \tfrac{1}{2}O_2 \rightarrow PMo_{10}V^{V}_2O_{40}^{5-} + H_2O$$

quantitatively and selectively dehydrogenated in two stages to the corresponding aldehydes or ketones via a Schiff-base imine intermediate, for example, for benzylamine eq 3.

$$ArCH_2NH_2 \xrightarrow{PVMo} [ArCH{=}NH] \xrightarrow[-NH_3]{+H_2O} ArCHO \xrightarrow[-H_2O]{+ArCH_2NH_2} ArCH{=}NCH_2Ar \quad (3)$$

$$ArCH{=}NCH_2Ar \xrightarrow[-ArCHO]{+H_2O} ArCH_2NH_2 \xrightarrow{PVMo} [ArCH{=}NH] \xrightarrow[-NH_3]{+H_2O} ArCHO$$

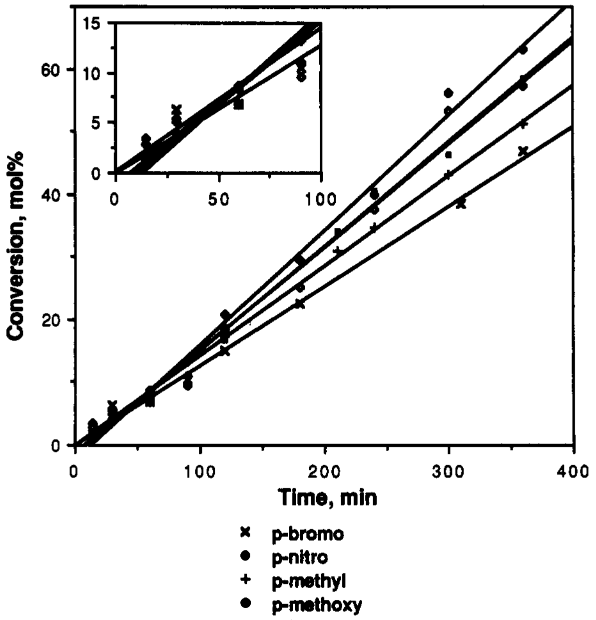

Figure 1. Reaction profile of benzyl alcohol oxidative dehydrogenation. Reaction conditions: 4 mmol of substrate, 12 mL of toluene, 0.04 mmol of 10% PVMo/C, 100 °C, 22 h, air 1 atm.

Table I. Oxidative Dehydrogenation of Benzylic Alcohols Catalyzed by 10% PVMo/C

substrate	product	yield,[a] mol %
benzyl alcohol	benzaldehyde	97[b]
benzyl alcohol	benzaldehyde	~2[c]
benzyl alcohol	benzaldehyde	94[d]
4-bromobenzyl alcohol	4-bromobenzaldehyde	96[b]
4-nitrobenzyl alcohol	4-nitrobenzaldehyde	93[b]
4-methoxybenzyl alcohol	4-methoxybenzaldehyde	94[b]
4-methylbenzyl alcohol	4-methylbenzaldehyde	98[b]
2-hydroxybenzyl alcohol	2-hydroxybenzaldehyde	0[e]
4-hydroxybenzyl alcohol	4-hydroxybenzaldehyde	0[e]
4-hydroxybenzyl alcohol	4-hydroxybenzaldehyde	0[f]
1-phenylethanol	acetophenone	94[b]

[a] Reaction conditions: 4 mmol of substrate, 12 mL of toluene, 0.04 mmol of 10% PVMo/C, 100 °C, 22 h, air 1 atm. Yields are based on substrate consumed and were computed by GLC analysis using a 10-m fused silica FFAP megabore column. [b] Only the specific product was formed, i.e., the selectivity was 100%. [c] Reaction under 1 atm nitrogen. [d] Reaction of reisolated catalyst. [e] Only unidentified tars were formed. [f] Reaction at 25 °C, substrate remained unchanged.

Results and Discussion

The vanadium–molybdenum heteropolyoxometallate, $Na_5PV_2Mo_{10}O_{40}$, prepared by the standard literature procedure[13] was impregnated on an activated carbon

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Table II. Oxidative Dehydrogenation of Alcohols Catalyzed by 10% PVMo/C

substrate	product	yield,[a] mol %
1-phenylethanol	acetophenone	94
2-octanol	2-octanone	8.3
3-heptanol	3-heptanone	4.8
cyclohexanol	cyclohexanone	3.6
2-phenylethanol	phenylacetaldehyde	0
1-octanol	1-octaldehyde	0

[a] Reaction conditions: 4 mmol of substrate, 12 mL of toluene, 0.04 mmol of 10% PVMo/C, 100 °C, 22 h, air 1 atm. Yields are based on substrate consumed, and the designated products were the only compounds formed.

support at a loading of 10% by weight yielding the supported catalyst, 10% PVMo/C. Oxidative dehydrogenation reactions were typically carried out by dissolving 4 mmol of the alcohol or amine substrate in 12 mL of toluene as solvent in the presence of 1 mol % heteropolyoxometallate under 1 atm of air at 100 ± 2 °C. Initial reaction profiles and final yields after 22 h for the dehydrogenation of benzylic alcohols to the corresponding aldehydes are given in Figure 1 and Table I, respectively. The results show practically quantitative yields for substrates with both electron-withdrawing and -donating ring substituents. Exceptional in this capacity are the hydroxybenzyl alcohols, which gave only unidentified tars whereas at ambient temperature no reaction took place. Reactions performed under a nitrogen atmosphere did not proceed significantly[14] beyond the stoichiometric amount of catalyst. A further and important observation was that no carboxylic acid products were observed, suggesting the absence or suppression of free-radical-type autoxidations, since autoxidations are significantly faster for aldehyde versus alcohol substrates.[15] The reaction kinetics, Figure 1, also show that the rate is zero order in the benzylic alcohol with little variability in the observed rate constant (k_{obs} = 0.15 - 0.20 mol s^{-1} mol-cat^{-1}) as a function of the substituent, probably indicating that the dehydrogenation step is not rate limiting for these substrates at the given conditions. This observation together with the fact that dioxygen is a required component lends credence to the generalized reaction scheme, eq 1, with the reoxidation of the catalyst as the rate-determining step. Catalyst reisolation after one reaction (Table I, entry 3) shows that the catalyst appears to be stable retaining its initial reactivity. In addition, UV–vis spectra of filtered reactions solutions showed no leached catalyst although some catalyst decomposition on the support cannot be ruled out.

For comparison, the possibility of performing the dehydrogenation reactions on nonbenzylic alcohols was also tested, Table II. The results show that secondary alcohols are only slightly but selectively dehydrogenated to ketones with the following relative reactivities 1-phenylethanol ≫ 2-octanol ~ 3-heptanol > cyclohexanol, whereas primary alcohols are inert.

Table III. Oxidative Dehydrogenation of Benzylic Amines Catalyzed by 10% PVMo/C

substrate	product	yield,[a] mol %	time,[b] h
$C_6H_5CH_2NH_2$	$C_6H_5CH{=}NCH_2C_6H_5$	100	0.5
	C_6H_5CHO	98	20
$C_6H_5CH_2NH_2$	C_6H_5CHO	2	20[c]
4-$MeOC_6H_4CH_2NH_2$	4-$MeOC_6H_4CH{=}NCH_2C_6H_4OMe$	100	0.5
	4-$MeOC_6H_4CHO$	97	20
4-$ClC_6H_4CH_2NH_2$	4-$ClC_6H_4CH{=}NCH_2C_6H_4Cl$	100	0.5
	4-ClC_6H_4CHO	98	20
$C_6H_5CH{=}NCH_2C_6H_5$	C_6H_5CHO, $C_6H_5CH_2NH_2$	2.5	20[c]
$C_6H_5CH{=}NCH_2C_6H_5$	C_6H_5CHO, $C_6H_5CH_2NH_2$	3.0	20[d]
$(C_6H_5CH_2)_2NH$	$C_6H_5CH{=}NCH_2C_6H_5$	86	3.0
	C_6H_5CHO	96	20
$C_6H_5CH_2NHCH_3$	$C_6H_5CH{=}NCH_3$	81	3.0
	C_6H_5CHO	90	20
$C_6H_5CH(CH_3)NH_2$	$C_6H_5C(CH_3){=}NCH(CH_3)C_6H_5$	95	1.0
	$C_6H_5COCH_3$	3.5	20
$(C_6H_5CH_2)_3N$	C_6H_5CHO	0	20

[a] Reaction conditions: 4 mmol of amine, 12 mL of toluene, 0.04 mmol of 10% PVMo/C, 100 °C, air 1 atm. Yields are based on substrate consumed and include all products. [b] The time given represents the time for optimal yield. [c] Reaction at 1 atm nitrogen. [d] In the absence of catalyst.

Table IV. Oxidative Dehydrogenation of Amines Catalyzed by 10% PVMo/C

substrate	product	yield,[a] mol %	time, h
c-$C_6H_{11}NH_2$	c-$C_6H_{10}O$	97	4.5
$CH_3(CH_2)_7NH_2$	$CH_3(CH_2)_6CHO$	56	
	$CH_3(CH_2)_6COOH$	38	7.0
$C_6H_5CH_2CH_2NH_2$	$C_6H_5CH_2COOH$	87	7.0
$(CH_3CH_2CH_2CH_2)_2NH$		0	20
$C_6H_5NH_2$		0	20

[a] Reaction conditions: 4 mmol of amine, 12 mL of toluene, 0.04 mmol of 10% PVMo/C, 100 °C, air 1 atm. Yields are based on substrate consumed and include all products.

After the original success in dehydrogenating benzylic alcohols, similar oxidative dehydrogenations were performed on benzylic amine substrates, Table III. Benzylamine and ring-substituted benzylic amines, $ArCH_2NH_2$, were quantitatively dehydrogenated within 20–30 min yielding exclusively the corresponding Schiff-base imines, $ArCH{=}NCH_2Ar$. The identity of the later was confirmed after isolation by MS and ^1H NMR. We believe these compounds are formed by dehydrogenation of the initial benzylamine to the highly unstable [ArCH=NH], which in the presence of trace amounts of water are hydrolyzed to benzaldehydes. The benzaldehydes are then immediately scavenged by yet unreacted benzylic amine yielding the Schiff base, eq 3. Further dehydrogenation of the Schiff base is continued slowly over a 24-h period to the final benzaldehyde product and is probably limited by slow Schiff-base hydrolysis coupled with fast amine dehydrogenation to benzaldehyde, which in the absence of amine yields the aldehyde as the exclusive product in quantitative yields. Control experiments run without catalyst or with catalyst under nitrogen (Table III, entries 5–6) to test if the supported heteropolyanion catalyzes the imine hydrolysis seem to indicate that the equilibrium reaction, eq 4, lies to the left. Under oxidative conditions the equilibrium is shifted by relatively fast dehydrogenation of any benzylamine formed.

$$C_6H_5CH{=}NCH_2C_6H_5 + H_2O \rightleftarrows C_6H_5CHO + C_6H_5CH_2NH_2 \quad (4)$$

Secondary benzylic amines such as dibenzylamine and N-methylbenzylamine undergo the same reaction although the initial formation of the Schiff base is much slower. The α-substituted α-methylbenzylamine reacts quickly to yield

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[14] The approximately 2% yield versus the 1% theoretical yield is probably due to incomplete purging of the activated carbon, which is a very effective adsorbant of molecular oxygen.

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the corresponding imine, $PhC(CH_3){=}NCH(CH_3)Ph$, which gives acetophenone only in limited amounts due to the higher stability of the Schiff base. Tribenzylamine is inert as may have been expected due to the absence of a hydrogen at the nitrogen blocking the potential dehydrogenation pathway. In contrast to the situation found for alcohols, primary aliphatic amines, Table IV, are effectively dehydrogenated, e.g., cyclohexylamine to cyclohexanone, octylamine to octaldehyde and octanoic acid, and phenylethylamine to phenylacetic acid. Significant amounts of acid are formed with primary acyclic amines as substrates because aliphatic aldehydes undergo oxidation much more easily than their aromatic counterparts. On the other hand, a simple secondary aliphatic amine such as di-*n*-butylamine is inert as is aniline, which lacks the required α-hydrogen. For the aliphatic amines no Schiff-base intermediates were formed (too unstable); thus, the overall reaction to the carbonyl compound is faster although the oxidative dehydrogenation reaction itself is slower than in the benzylamine case.

An active-carbon-supported molybdenum–vanadium heteropolyanion salt has been shown to be an effective and selective catalyst for the aerobic oxidative dehydrogenation of alcohols and amines. Further kinetic and spectroscopic research is under way in our laboratory in order to decipher the mechanism of these and similar reactions.

Experimental Section

Materials and Instruments. All reagents and solvents used were obtained commercially and were used without further purification. The activated carbon (Merck Catalog No. 2186) used was a fine powder. GLC measurements were made with a HP-5890 equipped with a FID detector and helium carrier gas. Peaks were quantified by a HP-3396 integrator after calibration with known reference compounds, except for the Schiff bases (see below). Mass spectra were taken on a HP5790 and ^1H NMR on a Brucker WP-200-SY spectrometer.

Catalyst Preparation. The $Na_5PV_2Mo_{10}O_{40}$ heteropolyanion salt was prepared by the common literature procedures.[13] The catalyst is in fact a hydrated mixture of stereoisomers and was identified by its ^{51}V NMR as previously described.[10] The heteropolyoxometallate was wet-impregnated onto the active carbon support by dissolving 1 gm of metalate in water and adding 9 gm of active carbon. The mixture was stirred for 30 min, and then the excess water was evaporated under reduced pressure. The catalyst was dried overnight in a vacuum oven (0.01 atm) at 80 °C. Karl Fisher titration showed that the 10% PVMo/C catalysts contained about 0.2 wt % water.

Typical Procedure for the Oxidative Dehydrogenation Reactions. The supported PVMo/C catalyst (0.04 mmol, 800 mg) was added to a solution of 4 mmol of benzyl alcohol in 12 mL of toluene in a magnetically stirred 25-mL flask. The mixture was heated to 100 °C in a thermostated oil bath and kept under a constant pressure of 1 atm of air by continuous flow air through the solution. Aliquots were removed from the reaction mixture and directly analyzed by GLC using a 10-m cross-linked (fused silica) FFAP megabore (i.d. 530 μm) column. Products and reactants were generally determined on a relative basis; however, to cross-check for noneluted products (none were indicated), bromobenzene was used as an external standard.

The identity of the Schiff bases was confirmed by isolation from the reaction mixture by catalyst filtration and solvent evaporation. For example, for benzylamine: MS 195, M (15), 194, M − 1 (17), 91, C_7H_7 (100); ^1H NMR at 200 MHz in $CDCl_3$ δ 8.35 (s, 1 H), 7.74 (m, 2 H), 7.32 (m, 8 H), 4.85 (s, 2 H).

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Registry No. $PMo_{10}V_2O_{40}$, 58071-93-5; $PhCH{=}NH$, 16118-22-2; $C_6H_5CH_2NH_2$, 100-46-9; 4-$MeOC_6H_4CH_2NH_2$, 2393-23-9; 4-$ClC_6H_4CH_2NH_2$, 104-86-9; $C_6H_5CH{=}NCH_2C_6H_5$, 780-25-6; $(C_6H_5CH_2)_2NH$, 103-49-1; $C_6H_5CH_2NHCH_3$, 103-67-3; $C_6H_5CH(CH_3)NH_2$, 98-84-0; $(C_6H_5CH_2)_3N$, 620-40-6; 4-$MeOC_6H_5CH{=}NCH_2$, 3261-60-7; $C_6H_5CH{=}NCH_3$, 622-29-7; $C_6H_5C(CH_3){=}NCH(CH_3)C_6H_5$, 25102-87-8; 4-$ClC_6H_4CH{=}NCH_2C_6H_4Cl$, 31264-06-9; c-$C_6H_{11}NH_2$, 108-91-8; $CH_3(CH_2)_7NH_2$, 111-86-4; $C_6H_5CH_2CH_2NH_2$, 64-04-0; $(CH_3CH_2CH_2CH_2)_2NH$, 111-92-2; $C_6H_5NH_2$, 62-53-3; c-$C_6H_{10}O$, 108-94-1; $CH_3(CH_2)_6CHO$, 124-13-0; $CH_3(CH_2)_6COOH$, 124-07-2; $C_6H_5CH_2COOH$, 103-82-2; benzyl alcohol, 100-51-6; 4-bromobenzyl alcohol, 873-75-6; 4-nitrobenzyl alcohol, 619-73-8; 4-methoxybenzyl alcohol, 105-13-5; 2-hydroxybenzyl alcohol, 90-01-7; 4-hydroxybenzyl alcohol, 623-05-2; 1-phenylethanol, 98-85-1; benzaldehyde, 100-52-7; 4-bromobenzaldehyde, 1122-91-4; 4-nitrobenzaldehyde, 555-16-8; 4-methoxybenzaldehyde, 123-11-5; acetophenone, 98-86-2; 2-octanol, 123-96-6; 3-heptanol, 589-82-2; cyclohexanol, 108-93-0; 2-phenylethanol, 60-12-8; 1-octanol, 111-87-5.

Kinetics and Mechanism of Ni(II) Ion Retarded Schiff-Base Hydrolysis of 2,2′-Dipyridylmethylideneaniline

Junghun Suh* and Dong Won Min

Department of Chemistry, Seoul National University, Seoul 151-742, Korea

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Nitrogen atoms of Schiff bases (imines) are weak bases and readily coordinate to metal ions. Imine bonds formed from amines and carbonyl compounds in the presence of metal ions are utilized as cyclizing linkages in a large number of macrocyclic complexes.[1]

Effects of metal ions acting as Lewis acid catalysts on organic reactions have been extensively investigated.[2-4] Although imines are labile and readily hydrolyzed, metal ions stabilize imine bonds present on macrocyclic rings. Whether metal ions stabilize or activate imine bonds in general, however, has not been systematically investigated. In this regard, we have performed kinetic studies on the hydrolysis of 2,2′-dipyridylmethylideneaniline (**1**), a nonmacrocyclic imine, in the presence of Ni(II) ion.

Results and Discussion

In the absence of Ni(II) ion, pseudo-first-order kinetics were observed for the hydrolysis of **1**, and the pseudo-first-order rate constants (k_o) measured therein at pH 2.3–5.2 are illustrated in Figure 1. Analysis of the pH profile according to Scheme I led to the values of pK_a = 3.40 and k_{lim} = 0.29 s^{-1}.

Scheme I

$$1 \underset{K_a}{\overset{H^+}{\rightleftharpoons}} 1H^+ \xrightarrow{k_{lim}} \text{products}$$

In the presence of Ni(II) ion, however, biphasic kinetics were observed with the relatively fast formation of an intermediate (spectrum b of Figure 2) from the substrate (spectrum a of Figure 2) and the subsequent slow conversion of the intermediate into the hydrolysis products (spectrum c of Figure 2). The addition of Ni(II) ion changes the UV–vis spectrum of **1** considerably. The spectrum of **1** (6×10^{-5} M), however, was identical in the presence of either 1 or 12 mM Ni(II), indicating that **1** is

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