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Direct Observation of Radical Intermediates While Investigating the Redox Behavior of Thiamin Coenzyme Models**

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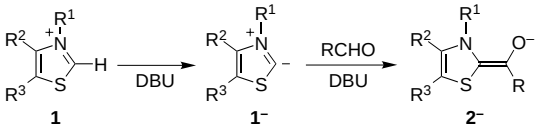
Thiamin diphosphate (ThDP) is the coenzyme for a number of important biochemical reactions, including the decarboxylation of pyruvic acid to acetaldehyde. The conjugate base of 2-hydroxyethyl-ThDP, which is an acyl carbanion equivalent and called an "active aldehyde", plays a key role in the catalysis of ThDP-dependent enzymes.[1] The active aldehyde is able to reduce various physiological electron acceptors, for example the lipoamide in the pyruvate dehydrogenase multienzyme complex,[2] the flavin adenine dinucleotide (FAD) in pyruvate oxidase,[3] and the Fe_4S_4 cluster in pyruvate-ferredoxin oxidoreductase.[4] Simple thiazolium ions have been studied extensively as models of the thiamin coenzyme, and valuable information about the elementary step of ThDP-dependent enzymatic reactions was provided.[5–10] The active aldehyde, however, readily undergoes acyloin-type condensation with a second pyruvate or aldehyde molecule in the absence of oxidizing agents.[1, 11] Such instability of the active aldehydes has precluded the direct determination of the most fundamental properties of the intermediates, such as oxidation potentials.[12] Therefore, no direct observation of the radical intermediates derived from thiamin coenzyme models has been described so far. Here we report the direct observation of radical intermediates of active aldehydes $\mathbf{2}^-$ with low-temperature cyclic voltammetry and EPR spectroscopy. Active aldehydes $\mathbf{2}^-$ are derived from 3-benzylthiazolium salts **1** and simple aldehydes such as acetaldehyde and benzaldehyde in the presence of 1,8-diazabicylco[5.4.0]undec-7-ene (DBU).

A cyclic voltammogram (CV) of the active aldehyde $\mathbf{2a}^-$—which is prepared in situ by adding neat DBU (1.0×10^{-2} M) to a deaerated solution of 3-benzylthiazolium ion **1a** ($5.0 \times$



a $R^1 = PhCH_2$, $R^2 = Me$, $R^3 = H$, R = Me
b $R^1 = PhCH_2$, $R^2 = R^3 = Me$, R = Me
c $R^1 = PhCH_2$, $R^2 = R^3 = H$, R = Me
d $R^1 = PhCH_2$, $R^2 = Me$, $R^3 = H$, R = Ph
e $R^1 = PhCH_2$, $R^2 = R^3 = Me$, R = Ph
f $R^1 = PhCH_2$, $R^2 = R^3 = H$, R = Ph
g $R^1 = PhCD_2$, $R^2 = Me$, $R^3 = H$, R = Me
h $R^1 = PhCH_2$, $R^2 = Me$, $R^3 = H$, $R = CD_3$
i $R^1 = PhCD_2$, $R^2 = Me$, $R^3 = H$, R = Ph

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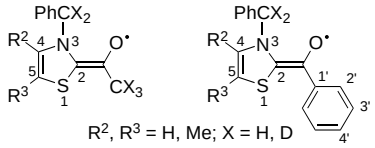
10^{-3} M), acetaldehyde (0.25 M), and 0.10 M tetrabutylammonium perchlorate (TBAP) in acetonitrile (MeCN) at 233 K—shows two reversible one-electron oxidations at $E^0_{ox} = -0.95$ and -0.74 V versus the saturated calomel electrode (SCE).[13] No reversible peaks can be observed at 298 K because of the fast acyloin condensation of $\mathbf{2a}^-$ with a second aldehyde molecule. Such a reversible CV at 233 K can be observed only in the presence of all the components (i.e., **1a**, DBU, and the aldehyde). This indicates that it is not the parent compound but the active aldehyde $\mathbf{2a}^-$ that undergoes the electrochemical redox reactions. The two one-electron oxidation potentials ($E^0_{ox(1)}$ and $E^0_{ox(2)}$) of various active aldehydes were also determined (Table 1). The $E^0_{ox(1)}$ and $E^0_{ox(2)}$ values of $\mathbf{2a}^- - \mathbf{2c}^-$, which are derived from acetaldehyde, are 200–300 mV more negative than those of active aldehydes $\mathbf{2d}^- - \mathbf{2f}^-$, which are derived from benzaldehyde. Substituents on the thiazolium rings have only minor effects on the oxidation potentials. The $E^0_{ox(1)}$ values in Table 1 support the proposal by Jordan et al. that the one-electron oxidation potential of the active aldehyde, which can reduce a flavin analogue, must be more negative than -0.67 V vs. SCE.[5e]



The observation of the well-defined one-electron redox couples indicates that a radical intermediate is formed in the first one-electron oxidation of the active aldehyde. Therefore, the EPR spectrum of a radical intermediate ($\mathbf{2}^\bullet$) generated by controlled-potential electrolysis was measured in deaerated MeCN (0.10 M TBAP) at 233 K. When the solution containing $\mathbf{2c}^-$ was electrolyzed at -1.20 or -0.50 V vs. SCE, there was no EPR signal. When the solution was electrolyzed at -0.80 V vs. SCE, however, a radical species with a g value of 2.0055 was detected at 233 K (Figure 1a). The observed spectrum can be simulated with the EPR parameters listed in Table 1 (Figure 1b).

The hyperfine splitting (hfs) constants of other active aldehyde radical species can also be determined in a similar manner (Table 1). The assignment of the hfs values indicates

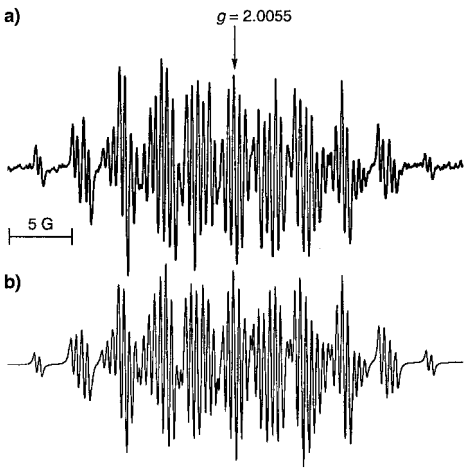


Figure 1. a) EPR spectum of $\mathbf{2c}^\bullet$ in MeCN at 233 K. b) The spectrum from a computer simulation; the hfs values used for the simulation are listed in Table 1.

that the detected radicals are neutral species ($\mathbf{2}^\bullet$). In the presence of a strong base such as DBU, the active aldehyde exists as an anion $\mathbf{2}^-$, since deprotonation of the OH group occurs. The first one-electron oxidation of $\mathbf{2}^-$ leads to the corresponding neutral radical species $\mathbf{2}^\bullet$, whose structure is similar to that suggested for the oxidized active aldehyde in pyruvate-ferredoxin oxidoreductase by Kerscher and Oesterhelt.[4b] The radical $\mathbf{2}^\bullet$ loses one more electron in the second oxidation step to form the 2-acylthiazolium ion $\mathbf{2}^+$. The assignments of $\mathbf{2}^\bullet$ in Table 1 are ensured by deuterium substitution at appropriate positions of the molecule. For example, deuterium substitution of the two hydrogen atoms at the benzylic positions of **1a** as well as that of the three hydrogen atoms of the acetyl moiety of $\mathbf{2a}^\bullet$ resulted in a drastic change in the splitting pattern. The hfs values of 2.34 and 3.46 G due to $PhCH_2$ and CH_3CO protons of $\mathbf{2a}^\bullet$ are decreased by a factor of 0.143, the magnetogyric ratio of proton to deuterium, to 0.33 and 0.51 G for $PhCD_2$ and CD_3CO deuterons of the corresponding deuterated radicals $\mathbf{2g}^\bullet$ and $\mathbf{2h}^\bullet$, respectively, when the other hfs values remain unchanged.[14]

Judging from the observed hfs values, the unpaired electron is highly delocalized in the active aldehyde moiety; the spin density is low only on C4. No appreciable change in the spin distribution is observed upon changing the substituents on the

Table 1. One-electron oxidation potentials $E^0_{ox(1)}$ and $E^0_{ox(2)}$ vs. SCE of active aldehydes $\mathbf{2}^-$,[a] g values, and hyperfine splitting (hfs) values of $\mathbf{2}^\bullet$.

	$E^0_{ox(1)}$ [V][b]	$E^0_{ox(2)}$ [V][b]	g [G]	hfs [G]						
				a_N(N)	a_H($PhCH_2$)	a_H(C-4)	a_H(C-5)	a_H(CH_3CO)	a_H(C-2′)	a_H(C-4′)
a	−0.98	−0.74	2.0052	4.74	2.34	0.64	3.12	3.46	–	–
b	−0.96	−0.73	2.0052	5.02	2.24	0.50	2.85	3.54	–	–
c	−0.93	−0.73	2.0055	4.87	2.65	0.38	3.00	3.45	–	–
d	−0.78	−0.44	2.0057	4.53	2.40	0.42	3.10	–	0.24	0.48
e	−0.79	−0.45	2.0051	4.70	2.20	0.45	2.64	–	0.24	0.48
f	−0.77	−0.42	2.0057	4.66	2.48	0.42	2.83	–	0.21	0.43
g	−0.95	−0.74	2.0052	4.74	0.33[c]	0.64	3.12	3.46	–	–
h	−0.95	−0.74	2.0052	4.74	2.34	0.64	3.12	0.51[c]	–	–
i	−0.78	−0.44	2.0057	4.53	0.34[c]	0.42	3.10	–	0.24	0.48

[a] Active aldehydes $\mathbf{2}^-$ were prepared from **1** (5.0×10^{-3} M), RCHO (0.25 M), and DBU (1.0×10^{-2} M) in deaerated MeCN containing 0.10 M TBAP at 233 K. [b] Working electrode: Pt, sweep rate: 0.10 V s^{-1}. [c] Deuterium splitting value.

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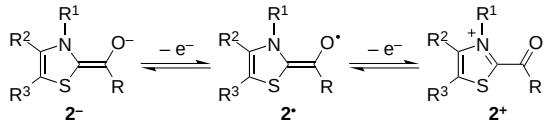
thiazolium ring. Therefore, the oxidative electron transfer processes of the active aldehyde can be described as shown in Scheme 1. The highly negative oxidation potentials of active



Scheme 1. Oxidation of active aldehydes $\mathbf{2}^-$ by two electron transfer steps.

aldehydes and the spin distribution of the intermediate radicals determined for the first time in this study provide the energetic basis for the ThDP-dependent electron transport systems as well as valuable mechanistic insight into the enzymatic reactions.

Experimental Section

Thiazoles, benzyl bromide, acetaldehyde, and benzaldehyde were purchased from Tokyo Chemical Industry and used as received. MeCN was purified and dried with CaH_2 by the standard procedure.[15] TBAP was recrystallized from ethanol and dried in vacuum at 40 °C prior to use. 3-Benzylthiazolium bromide was prepared by the reaction of the corresponding thiazole with benzyl bromide at 80 °C, and purified by recrystallization from acetone. Cyclic voltammetry measurements were performed on a BAS 100B electrochemical analyzer with solutions in deaerated MeCN containing 0.10 M TBAP as supporting electrolyte. The Pt working electrode (BAS) was polished with a BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to the Ag/$AgNO_3$ (0.01 M) reference electrode and converted into values versus SCE by adding 0.29 V.[16] All electrochemical measurements were carried out under an atmospheric pressure of argon. EPR spectra were recorded on a JEOL JES-RE1XE instrument under nonsaturating microwave power conditions. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise (S/N) ratio of the observed spectra. The *g* values and hyperfine splitting (hfs) constants were calibrated with a Mn^{2+} marker. Computer simulations of the EPR spectra were carried out with the program Calleo ESR Version 1.2 (Calleo Scientific) on a Macintosh personal computer.

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Generation of "Naked" Fluoride Ions in Unprecedentedly High Concentrations from a Fluoropalladium Complex**

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Since the discovery of the first reliable sources of weakly solvated ("naked") fluoride ions,[1, 2] a number of intriguing reactivity patterns and applications of the F^- ion in synthesis have been reported which clearly indicate its extraordinarily strong basicity and nucleophilicity in media of low polarity.[1–8] However, the number of sources for "genuinely naked" F^-

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