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Acid-Catalyzed One-Electron Reduction of Nitrite to Nitric Oxide by an NADH Analog and 1,1'-Dimethylferrocene in the Absence and Presence of Dioxygen

Shunichi FUKUZUMI* and Tomohiro YORISUE
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565

One-electron reduction of nitrite to nitric oxide proceeds efficiently by an acid-stable NADH analog, 9,10-dihydro-10-methylacridine (two-electron reductant) as well as 1,1'-dimethylferrocene (one-electron reductant) in the presence of perchloric acid in acetonitrile. The effects of dioxygen on both the one-electron and two-electron reductant systems are compared.

Mechanisms of the enzymatic reduction of nitrite especially those of denitrification[1)] as well as the effect of dioxygen[2)] have recently attracted considerable interest. In the enzymatic nitrite reduction, dihydronicotinamide adenine dinucleotide (NADH) being a two-electron reductant is used as a common electron source.[3)] However, no nonenzymatic reduction of nitrite by NADH analogs has so far been reported, although electrocatalytic reduction of nitrite[4)] as well as the reduction by various inorganic one-electron reductants[5)] has been studied extensively. This study reports efficient one-electron reduction of nitrite by an acid-stable NADH analogue, 9,10-dihydro-10-methylacridine (two-electron reductant)[6)] as well as 1,1'-dimethylferrocene (one-electron reductant)[7)] in the presence of perchloric acid ($HClO_4$) in acetonitrile (MeCN), comparing the effects of dioxygen on both the two-electron and one-electron reductant systems.

No oxidation of 9,10-dihydro-10-methylacridine ($AcrH_2$) or 1,1'-dimethylferrocene [$Fe(C_5H_4Me)_2$] by nitrite (NO_2^-) has been observed in MeCN at 298 K. The addition of $HClO_4$ to the $AcrH_2$-NO_2^- and $Fe(C_5H_4Me)_2$-NO_2^- systems, however, results in the facile oxidation of $AcrH_2$ and $Fe(C_5H_4Me)_2$ to yield 10-methylacridinium ion ($AcrH^+$) and 1,1'-dimethylferrocenium ion [$Fe(C_5H_4Me)_2^+$], respectively. The stoichiometries of the reactions were determined from the spectral titrations.[8)] In each case, one-electron reduction of NO_2^- occurs to yield NO; a two-electron reductant ($AcrH_2$) and a one-electron reductant $[Fe(C_5H_4Me)_2]$ reduce two- and one-equivalent NO_2^- (Eqs. 1 and 2,

$$AcrH_2 + 2NO_2^- + 3H^+ \longrightarrow AcrH^+ + 2NO + 2H_2O \quad (1)$$

$$Fe(C_5H_4Me)_2 + NO_2^- + 2H^+ \longrightarrow Fe(C_5H_4Me)_2^+ + NO + H_2O \quad (2)$$

respectively.[9] Rates of the oxidation of $AcrH_2$ and $Fe(C_5H_4Me)_2$ by $NaNO_2$ in the presence of excess $HClO_4$ in MeCN containing H_2O (2.8 and 5.6 M) were monitored by the increase in the absorbance at λ_{max} 358 and 650 nm due to the formation of $AcrH^+$ and $Fe(C_5H_4Me)_2^+$, respectively, using a stopped flow spectrophotometer. In the absence of H_2O, the rates were too fast to be followed by the conventional stopped flow technique. Rates of both reactions obey clean second-order kinetics, showing a first-order dependence on the concentration of each reactant in the presence of excess $HClO_4$ in MeCN containing H_2O. The observed second-order rate constants k_{obsd} increase with an increase in the $HClO_4$ concentration and both k_{obsd} values of $AcrH_2$ and $Fe(C_5H_4Me)_2$ show a first-order dependence on $[HClO_4]$ in the low concentration region, changing to second-order dependence in the higher concentration region, as shown in Fig. 1.[10] Such an identical change for different reductants in the order with respect to $[HClO_4]$ may reflect a change in the primary oxidant, i.e., from nitrous acid (HONO) to nitrosonium ion (NO^+) as given by Eqs. 3 and 4,

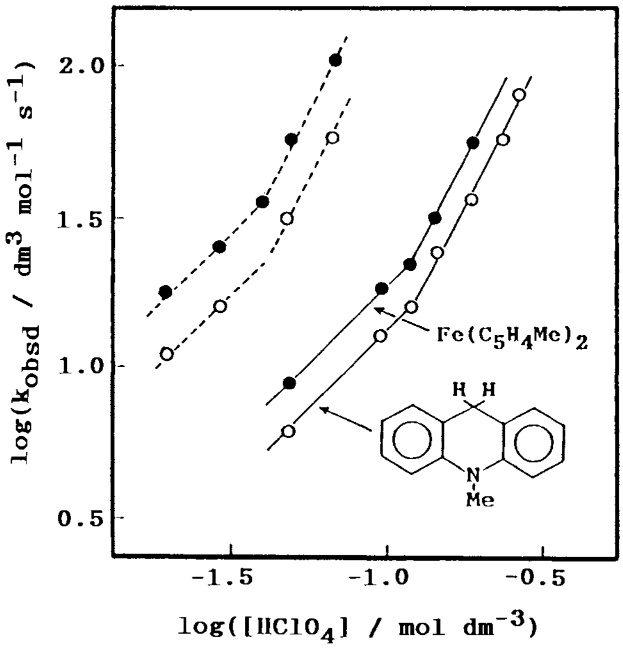


Fig. 1. Plots of log k_{obsd} vs. log$[HClO_4]$ for the reduction of $NaNO_2$ ($1.0 \times 10^{-3} - 1.0 \times 10^{-2}$ mol dm^{-3}) by $AcrH_2$ (o ; $5.0 \times 10^{-5} - 2.0 \times 10^{-4}$ mol dm^{-3}), and $Fe(C_5H_4Me)_2$ (● ; $1.0 \times 10^{-3} - 1.0 \times 10^{-2}$ mol dm^{-3}) in the presence of $HClO_4$ in MeCN containing 5.6 (——) and 2.8 mol dm^{-3} (---) H_2O at 298 K.

$$NO_2^- + H^+ \rightleftharpoons HONO \quad (3) \qquad HONO + H^+ \rightleftharpoons NO^+ + H_2O \quad (4)$$

respectively, since the protonation of HONO is known to yield NO^+.[11] The one-electron reduction of nitrite to nitric oxide by both $AcrH_2$ and $Fe(C_5H_4Me)_2$ may proceed *via* electron transfer to HONO or NO^+.[12] In fact, electron transfer from both $AcrH_2$ and $Fe(C_5H_4Me)_2$ to NO^+ is highly exothermic judging from the one-electron oxidation potentials of $AcrH_2$ (E^0_{ox} =

0.80 V _vs_. SCE)[13] and $Fe(C_5H_4Me)_2$ (E^0_{ox} = 0.26 V _vs_. SCE)[7] and the one-electron reduction potential of NO^+ (E^0_{red} = 0.88 V _vs_. ferrocene, E^0_{ox} of ferrocene = 0.37 V vs. SCE).[14] The increase in the concentration of H_2O may cause the decrease in the NO^+ concentration (Eq. 4), resulting in the decrease in the rate constant as observed in Fig. 1.

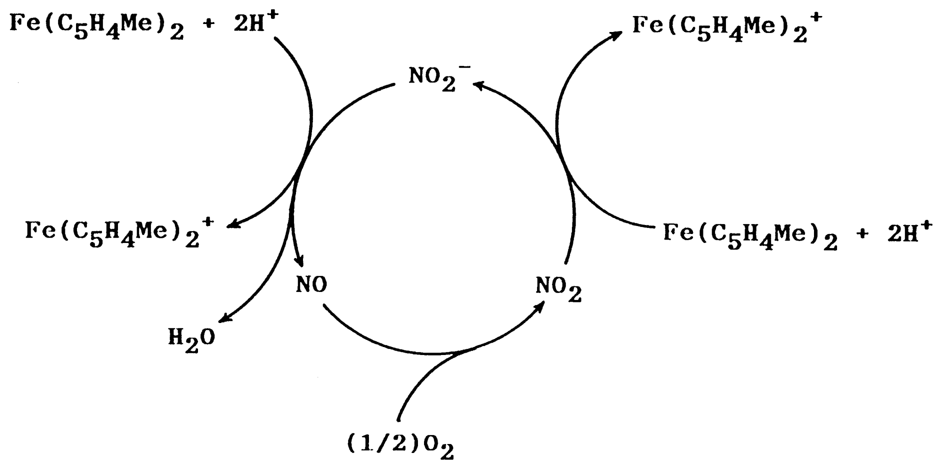
In the presence of O_2 (2.6 x 10^{-3} mol dm^{-3}), the concentrations of $AcrH^+$ formed were the same as those of the initial concentrations of $NaNO_2$ (< 2.6 x 10^{-3} mol dm^{-3}) in the presence of excess $AcrH_2$ (> [$NaNO_2$]) and $HClO_4$ (0.58 mol dm^{-3}). Thus, the stoichiometry of the reaction (Eq. 1) is changed to Eq. 5, where $AcrH_2$ reacts with equivalent NO_2^- to yield HNO_3.

$$AcrH_2 + NO_2^- + O_2 + 2H^+ \longrightarrow AcrH^+ + HNO_3 + H_2O \qquad (5)$$

In this case, the two-electron oxidation of $AcrH_2$ is accompanied by the two-electron oxidation of NO_2^- to HNO_3 and the four-electron reduction of O_2 to H_2O. Such a clean change of the stoichiometry in the presence of O_2 may be caused by the following reaction sequence; the facile oxidation of NO by O_2 occurs to yield NO_2 (Eq. 6) which dimerizes and hydrolyzes to nitrous and nitric acid (Eq. 7). The combination of Eqs. 1, 6, and 7

$$NO + (1/2)O_2 \longrightarrow NO_2 \qquad (6) \qquad\qquad 2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3 \qquad (7)$$

gives the net stoichiometry (Eq. 5). In contrast, the four-electron reduction of dioxygen by $Fe(C_5H_4Me)_2$ occurs efficiently in the presence of a catalytic amount of nitrite in MeCN containing $HClO_4$.[15] In the case of $Fe(C_5H_4Me)_2$ electron transfer to NO_2 may be exothermic judging from the one-electron reduction potential of NO_2 (E^0_{red} = 0.320 V _vs_. ferrocene),[14] although the electron transfer from $AcrH_2$ (E^0_{ox} = 0.80 V _vs_. SCE)[13] may be endothermic. Thus, electron transfer from $Fe(C_5H_4Me)_2$ to NO_2 may proceed efficiently before the dimerization and hydrolysis (Eq. 7) occur, accompanied by the regeneration of nitrite as shown below.



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8) Spectral titrations were carried out by determining the concentrations of $AcrH^+$ and $Fe(C_5H_4Me)_2{}^+$ formed when the initial ratios of $AcrH_2/NaNO_2$ and $Fe(C_5H_4Me)_2/NaNO_2$ were changed in the presence of excess $HClO_4$ (0.10 or 1.0 mol dm^{-3}) in MeCN, respectively.
9) The amount of NO formed was determined by the absorbance at λ_{max} 450 nm due to $Fe(NO)^{2+}$ formed by the addition of $Fe(ClO_4)_2$ to the reaction mixture.[5)]
10) The least-squares analysis of the plots in Fig. 1 gives the slopes of 1.02 $\pm$ 0.05 and 1.93 $\pm$ 0.07 for the first-order and second-order dependence, respectively.
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12) The second electron transfer from $AcrH^{\cdot}$, formed by deprotonation of $AcrH_2{}^{+\cdot}$ to HONO or NO^+ may be much faster as compared with $AcrH_2$.
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15) The stoichiometry was confirmed by spectral titration; four-equivalent $Fe(C_5H_4Me)_2$ reacts with O_2 (2.6×10^{-3} mol dm^{-3}) and four-equivalent H^+ in the presence of a catalytic amount of $NaNO_2$ (1×10^{-4} mol dm^{-3}) in the presence of $HClO_4$ (0.47 mol dm^{-3}) in MeCN to yield $Fe(C_5H_4Me)_2{}^+$.

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