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Autocatalytic Reduction of Nitric Acid by an Acid-Stable NADH Analogue

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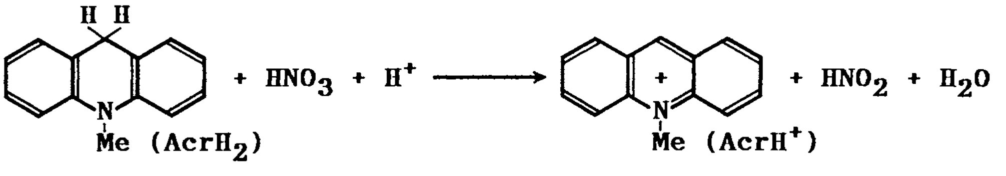
The reduction of nitric acid to nitrous acid by an acid-stable NADH analogue proceeds autocatalytically in the presence of perchloric acid in acetonitrile <u>via</u> novel chain reactions where the reduction of one nitrous acid in the presence of nitric acid eventually results in the formation of two nitrous acid.

The reduction of nitrate (NO_3^-) to nitrite (NO_2^-) is catalyzed in nature by the enzyme nitrate reductase.[1] NADH is a common source of reducing equivalents for NO_3^- reduction in the enzymatically catalyzed reactions.[1] Substantial efforts have been directed toward the nonenzymatic reduction of NO_3^- by electrochemical and photochemical methods.[2,3] However, no nonenzymatic reduction of NO_3^- by NADH or the analogues has so far been reported. Here we report that an acid-stable NADH analogue, 9,10-dihydro-10-methylacridine ($AcrH_2$),[4] can reduce NO_3^- to NO_2^- efficiently in the presence of $HClO_4$ in MeCN <u>via</u> novel autocatalytic reactions.

No oxidation of $AcrH_2$ by NO_3^- has been observed in deaerated MeCN in the dark at 298 K. The addition of $HClO_4$ (70%, 2.0 mol dm^{-3}) to the deaerated MeCN solution containing $AcrH_2$ (4.0×10^{-3} mol dm^{-3}) and $NaNO_3$ (0.10 mol dm^{-3}), however, results in the facile oxidation of $AcrH_2$ by HNO_3 to yield 10-methylacridinium ion ($AcrH^+$) and HNO_2 (Eq. 1). The yield of HNO_2 was the same as that of $AcrH^+$.[5] The reaction was monitored spectrophotometrically at 358 nm, where the absorbance of species other than $AcrH^+$ is negligible, by using a quartz cuvette (4.6 cm^3) containing a 2.4 cm^3 MeCN solution. A typical time course is shown in Fig. 1, where the



(1)

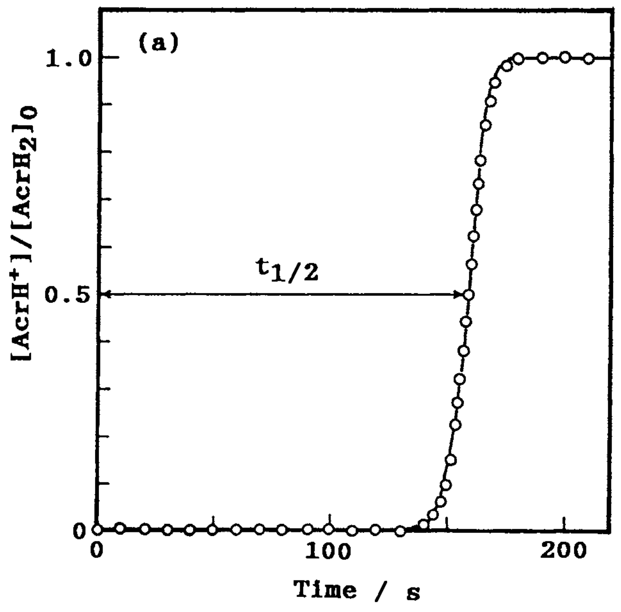


Fig. 1. Time dependence for the reduction of $NaNO_3$ (0.16 mol dm^{-3}) by $AcrH_2$ (8.0×10^{-4} mol dm^{-3}) in the presence of $HClO_4$ (1.0 mol dm^{-3}) in MeCN at 298 K. The calculated time dependence (o) is obtained by using Eq. 4. with $t_{1/2}$ = 159 s and c = 0.25 s^{-1}.

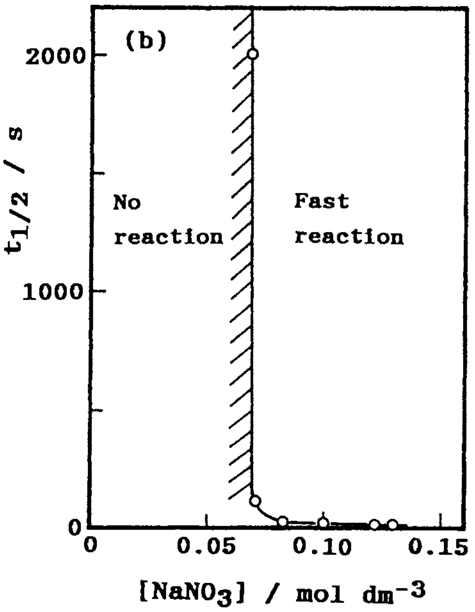


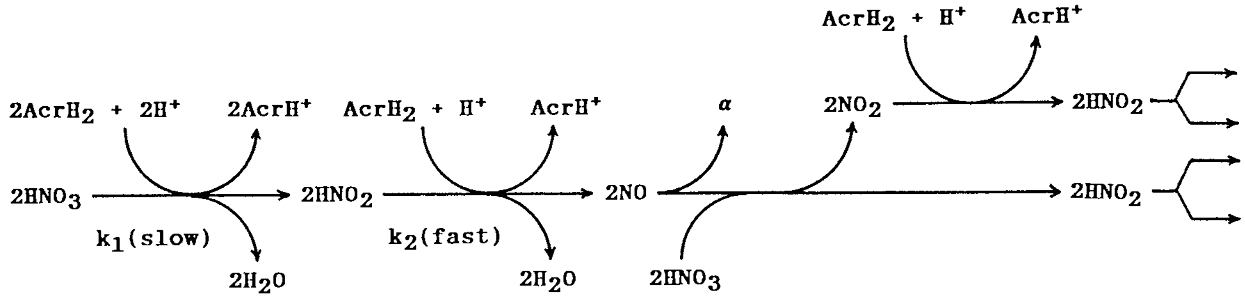
Fig. 2. Plot of the half-life ($t_{1/2}$) vs. $[NaNO_3]$ for the reduction of $NaNO_3$ by $AcrH_2$ (5.0×10^{-4} mol dm^{-3}) in the presence of $HClO_4$ (2.0 mol dm^{-3}) in MeCN at 298 K.

very slow rise in absorbance is followed by a rapid autocatalytic buildup of $AcrH^+$. In such a case the half-life of the reaction ($t_{1/2}$) is approximately equal to the time when the rapid buildup starts. The $t_{1/2}$ value is extremely sensitive to the initial concentration of NO_3^- in the presence of excess $HClO_4$. The dependence of $t_{1/2}$ on $[NaNO_3]$ in the presence of $HClO_4$ (2.0 mol dm^{-3}) is shown in Fig. 2, where a sharp dropoff of $t_{1/2}$ is observed at $[NaNO_3] > 7.0 \times 10^{-2}$ mol dm^{-3}. In the region $[NaNO_3] < 7.0 \times 10^{-2}$ mol dm^{-3}, no reaction has taken place at all. The value of such a critical concentration $[NaNO_3]_c$ is independent of $[HClO_4]$ which is in excess to $[NaNO_3]$. However, the $[NaNO_3]$ is very sensitive to the volume of the gas phase of the cuvette. As such no critical concentration of $NaNO_3$ has been observed, when the cuvette was filled with the reactant solution. The addition of a catalytic amount of $NaNO_2$ also causes the drastic decrease in the $t_{1/2}$ value.

We have recently reported that NO_2^- is readily reduced by $AcrH_2$ in the presence of $HClO_4$ in MeCN to yield NO and $AcrH^+$ (Eq. 2).6) On the other

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

hand, NO is known to react with NO_3^- in the presence of an acid to yieldNO$_2$ and HNO_2.[7] Thus, based on the above results, the autocatalytic reduction of HNO_3 by $AcrH_2$ may proceed as shown in Scheme 1. The reaction may start by the acid-catalyzed reduction of HNO_3 to HNO_2 by $AcrH_2$. This step must be quite slow judging from the very slow initial buildup of $AcrH^+$ (Fig. 1). Once HNO_2 is formed, a rapid autocatalytic buildup of HNO_2 may occur via the facile one-electron reduction of HNO_2 to NO by $AcrH_2$,[6] followed by the fast reaction of NO with HNO_3 to yield NO_2,[7] regenerating HNO_2 (Scheme 1). Since NO_2 is also readily reduced by $AcrH_2$ in the presence of $HClO_4$ to give another HNO_2 molecule, the initial formation of one HNO_2 molecule results in the formation of two HNO_2 molecules (Scheme 1). Thus, the autocatalytic reduction of HNO_3 by $AcrH_2$ may proceed via chain reactions where HNO_2 plays the pivotal role in determining the kinetics of the overall reaction. This may be the reason why the initial addition of a catalytic amount of HNO_2 causes the drastic decrease in the $t_{1/2}$ value.



Scheme 1.

According to Scheme 1, the rate of formation of $AcrH^+$ is given by Eq. 3, where k_1 and k_2 are the rate constants of the initial slow reduction of HNO_3 and the subsequent fast reduction of HNO_2, respectively.

$$d[AcrH^+]/dt = [AcrH_2](k_1[HNO_3] + 2k_2[HNO_2]) \qquad (3)$$

Since $[AcrH_2] = [AcrH_2]_0 - [AcrH^+]$, $[HNO_2] = [AcrH^+]$, and $[HNO_3] >> [AcrH_2]$, Eq. 3 is readily solved to yield Eq. 4, where $c_1 = k_1[HNO_3] + 2k_2[AcrH_2]_0$ and the half-life ($t_{1/2}$) is given by $c^{-1}\ln(2k_2[AcrH_2]_0/k_1[HNO_3])$ under the conditions that $2k_2[AcrH_2] >> k_1[HNO_3]$.

$$[AcrH^+]/[AcrH_2]_0 = [\exp(ct) - 1]/[\exp(ct) + \exp(ct_{1/2})] \qquad (4)$$

The calculated time dependence based on Eq. 4 agrees well with the experimental result of the rapid and sudden buildup of $AcrH^+$ as shown in Fig. 1, demonstrating the validity of the kinetic formulation (Eq. 3).

If a tiny fraction of NO (α) is escaped from the solution to the gas phase (Scheme 1), Eq. 3 is rewritten by Eq. 5, where $[AcrH^+] = [HNO_2] +$

$$d[AcrH^+]/dt = [AcrH_2]\{k_1[HNO_3] + 2k_2([AcrH^+] - 3\alpha/2)\} \qquad (5)$$

$(3/2)\alpha$. In such a case no rapid buildup of $AcrH^+$ may take place under the conditions that $[HNO_3] < (3k_2/k_1)\alpha$, since the rate of formation of $AcrH^+$ becomes zero when $[AcrH^+]$ reaches the value $(3/2)\alpha - (k_1/2k_2)[HNO_3]$. Under the conditions that $[HNO_3] > (3k_2/k_1)\alpha$, the reaction undergoes to completion.[8] This may be the reason why there exists the critical concentration of HNO_3 for the reaction as shown in Fig. 2, but why such a critical phenomenon disappears when the reaction cuvette is filled with the solution.

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5) The HNO_2 formed was separated from $AcrH^+$ by isolating as $AgNO_2$ by adding $AgNO_3$ to the resulting solution after neutralization with NaOH. Then, the yield of HNO_2 was determined by the absorption spectrum (λ_{max} = 372 nm, ε_{max} = 55.9 dm^3 mol^{-1} cm^{-1}).
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8) Only a trace amount of NO was detected in the gas phase of the cuvette by the glc analysis, indicating that $k_2 \gg k_1$.

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