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Photoinduced Hydride Reduction of an NAD^+ Analogue with Permethylpolysilanes Acting as Electron Sources and Water as a Proton Source

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Photoinduced hydride reduction of an NAD^+ analogue, 10-methylacridinium ion with permethylpolysilanes [$Me_3SiSiMe_3$, $Me(SiMe_2)Me$, $(Me_2Si)_6$] acting as electron sources and water as a proton source occurs efficiently in acetonitrile under irradiation of visible light (λ > 360 nm) to yield 9,10-dihydro-10-methylacridine selectively.

Reduction of nicotinamide adenine dinucleotide (NAD^+) as well as oxidation of the reduced form (NADH) is one of the most fundamental processes of biological redox reactions.[1)] Most reducing agents used so far for two-electron reduction of NAD^+ analogues are hydride donors which transfer a hydride ion (equivalent to two electrons and a proton) directly to NAD^+ analogues.[2-4)] However, no reducing agents providing two electrons and a proton separately have so far been known other than dithionite which acts as a two-electron donor in the hydride reduction of NAD^+ analogues, when a proton is provided separately from water.[5)] This study reports that permethylpolysilanes, which are known as unique σ-electron donors,[6)] can act as two-electron donors in the photoinduced hydride reduction of an NAD^+ analogue, 10-methylacridinium ion ($AcrH^+$), when a proton is provided separately from water, to yield the corresponding NADH analogue, 9,10-dihydro-10-methylacridine ($AcrH_2$).

Irradiation of the absorption band of $AcrH^+ClO_4^-$ (λ_{max} 358 nm) in dehydrated MeCN containing $Me_3SiSiMe_3$ results in the increase in the absorbance at 292 nm with a clean isosbestic point as shown in Fig. 1.

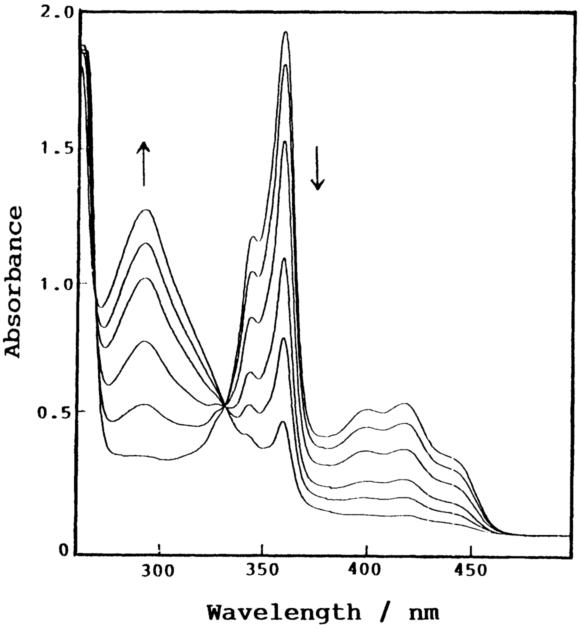
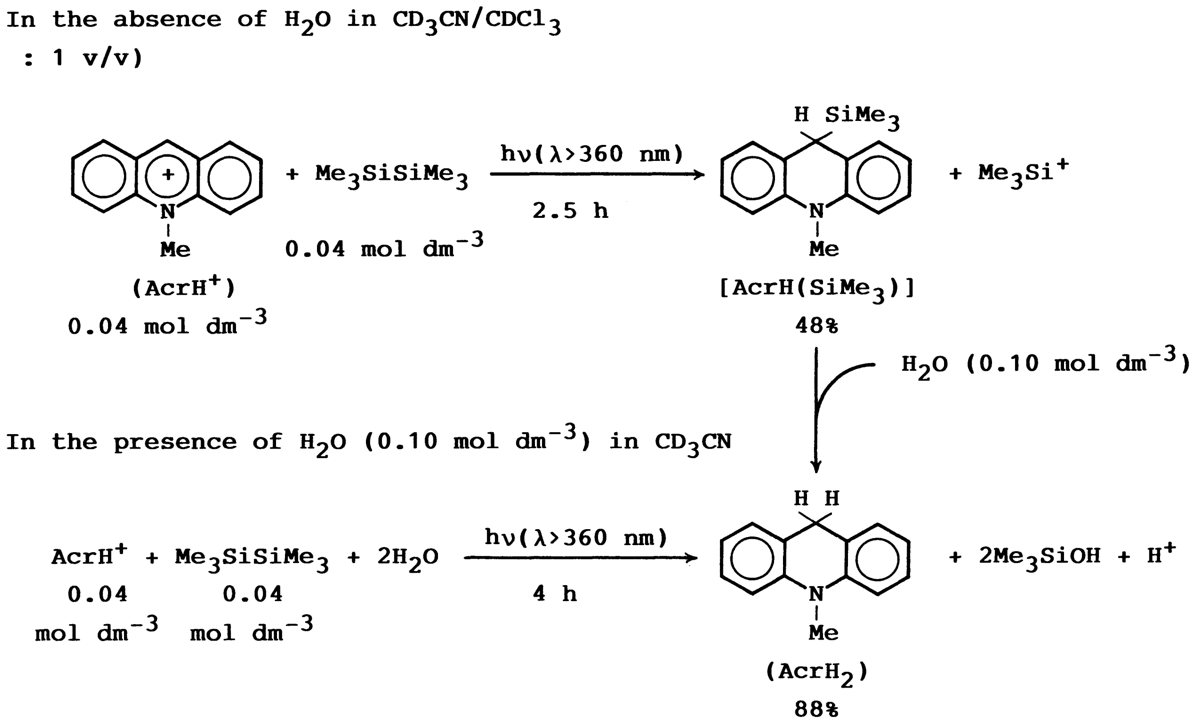


Fig. 1. Electronic absorption spectra observed in photoreduction of $AcrH^+$ (1.0×10^{-4} mol dm^{-3}) by $Me_3SiSiMe_3$ (5.0×10^{-2} mol dm^{-3}) in dry deaerated MeCN at 298 K (30-120 s interval).



Scheme 1.

The products were identified as 9,10-dihydro-9-trimethylsilyl-10-methylacridine [AcrH(SiMe$_3$)] and trimethylsilyl cation (Me_3SiClO_4) by the ^{1}H NMR spectra which were measured after visible light irradiation (λ > 360 nm) of a $CD_3CN/CDCl_3$ (1 : 1 v/v) solution containing AcrH$^+$ (0.04 mol dm^{-3}) and $Me_3SiSiMe_3$ (0.04 mol dm^{-3}).$^{7,8)}$ The addition of water to the resulting solution yields AcrH$_2$ as shown in Scheme 1.$^{7)}$ When the photochemical reaction of AcrH$^+$ with $Me_3SiSiMe_3$ is carried out in MeCN containing H_2O initially, the overall hydride reduction of AcrH$^+$ occurs to yield AcrH$_2$ selectively (Scheme 1).$^{9)}$ Such photoinduced hydride reduction of AcrH$^+$ occurs also with $Me(SiMe_2)_3Me$ and $(Me_2Si)_6$ which act as two-electron donors and a proton is provided separately from H_2O. The quantum yields (Φ) were determined using a ferrioxalate actinometer with 358 nm irradiation. The Φ value increases with an increase in the concentration of permethylpolysilanes, [Si-Si], to approach a limiting (Φ_∞) value in accordance with Eq. 1,

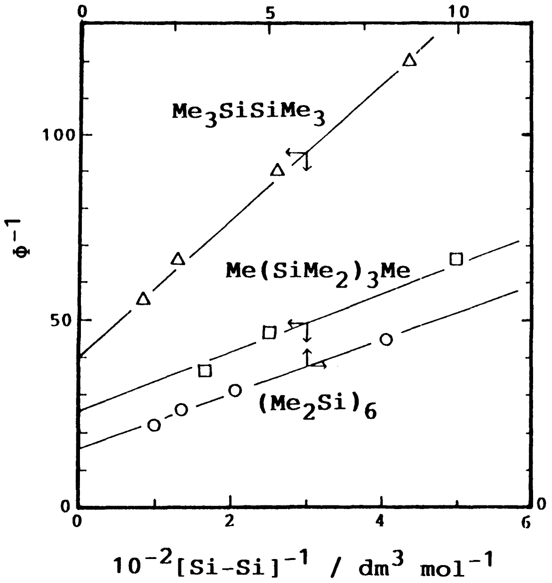


Fig. 2. Plots of Φ^{-1} vs. $[\mathrm{Si\text{-}Si}]^{-1}$ for the photoreduction of AcrH$^+$ by permethylpolysilanes in dry deaerated MeCN at 298 K.

$$\Phi^{-1} = \Phi_\infty^{-1}[1 + (K_{obs}[\mathrm{Si\text{-}Si}])^{-1}] \qquad (1)$$

Table 1. Limiting Quantum Yields Φ_∞, the Observed Quenching Constants K_{obs}, and the Rate Constants k_{obs} in the Photoreduction of $AcrH^+$ by Permethylpolysilanes, and the Fluorescence Quenching Rate Constants k_q of $^1AcrH^{+*}$ by Permethylpolysilanes in MeCN at 298 K

Permethyl-polysilanes	Φ_∞ a)	K_{obs} a) $dm^3\ mol^{-1}$	k_{obs} b) $dm^3\ mol^{-1}\ s^{-1}$	k_q $dm^3\ mol^{-1}\ s^{-1}$
$Me_3SiSiMe_3$	0.038	2.2×10^2	7.1×10^9	7.1×10^9
$Me(SiMe_2)_3Me$	0.049	4.4×10^2	1.4×10^{10}	1.4×10^{10}
$(MeSi)_6$	0.073	6.9×10^2	2.2×10^{10}	2.3×10^{10}

a) Determined by Eq. 1. b) Determined by the relation, $k_{obs} = K_{obs}\tau^{-1}$ (τ = 31 ns).

where K_{obs} is the quenching constant of the excited state of $AcrH^+$ in the photoreduction of $AcrH^+$. The linear plots of Φ^{-1} vs. $[Si\text{-}Si]^{-1}$ are shown in Fig. 2. From the slopes and intercepts are obtained the Φ_∞ and k_{obs} values, which are listed in Table 1.

Irradiation of the absorption band of $AcrH^+$ causes fluorescence at 490 nm in MeCN. The fluorescence of $^1AcrH^{+*}$ is quenched efficiently by permethylpolysilanes. The quenching rate constants k_q were determined from the slopes of the Stern-Volmer plots and the lifetime of the singlet excited state $^1AcrH^{+*}$ (τ 31 ns).[2] The k_q values are also listed in Table 1, where k_q value increases in the order $Me_3SiSiMe_3$ < $Me(SiMe_2)_3Me$ < $(MeSi)_6$, in accordance with the order of the electron-donor ability.[6,10] Thus, the fluorescence quenching of $^1AcrH^{+*}$ by permethylpolysilanes may occur by electron transfer from permethylpolysilanes to $^1AcrH^{+*}$.

The k_{obs} values obtained from the plots in Fig. 2 by assuming that the excited state of $AcrH^+$ involved in the photochemical reaction is singlet ($^1AcrH^{+*}$; $k_{obs} = K_{obs}\tau^{-1}$, τ = 31 ns) agree well with the k_q values determined independently by the fluorescence quenching of $^1AcrH^{+*}$ (Table 1). Thus, the photoreduction of $AcrH^+$ may proceed via electron transfer from permethylpolysilanes (e.g., $Me_3SiSiMe_3$) to the singlet excited state, $^1AcrH^{+*}$. Since one-electron oxidation of $Me_3SiSiMe_3$ is known to result in the facile cleavage of the Si-Si bond to yield Me_3Si^+ and $Me_3Si\cdot$,[11] electron transfer from $Me_3SiSiMe_3$ to $^1AcrH^{+*}$ may give the singlet radical pair, followed by the radical coupling between $Me_3Si^\cdot$ and $AcrH^\cdot$ to yield Me_3SiClO_4 and $AcrH(SiMe_3)$ selectively (Eq. 2). Then, the facile hydrolysis of Me_3SiClO_4 may occur in the presence of H_2O to yield the silanol and perchloric acid (Eq. 3),[9] followed by the acid cleavage of the Si-C bond of $AcrH(SiMe_3)$ to yield $AcrH_2$ (Eq. 4).[12] The stoichiometry of such overall photoinduced hydride reduction

$$\begin{aligned} &Me_3SiSiMe_3 + {}^1AcrH^{+*} \longrightarrow {}^1(Me_3SiSiMe_3^{+\cdot}\ AcrH^\cdot) \longrightarrow {}^1(Me_3Si^+\ Me_3Si^\cdot\ AcrH^\cdot) \\ &\qquad \longrightarrow Me_3Si^+ + AcrH(SiMe_3) \qquad (2) \end{aligned}$$

$$Me_3SiClO_4 + H_2O \longrightarrow Me_3SiOH + HClO_4 \qquad (3)$$

$$\mathbf{AcrH(SiMe_3) + HClO_4 \longrightarrow AcrH_2 + Me_3SiClO_4} \qquad \mathbf{(4)}$$

of $AcrH^+$ by $Me_3SiSiMe_3$ agrees with that in Scheme 1.

In conclusion, permethylpolysilanes can be used as unique sources of a hydride ion, consisting of two electrons and a proton, which are provided separately by permethylpolysilanes and water, respectively (Eqs. 2-4).

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