Photo-induced One-electron Reduction of 10-Methylacridinium Ion with Group 14 Dimetallic Compounds using Visible Irradiation

Shunichi Fukuzumi,*[a] Toshiaki Kitano,[a] and Kunio Mochida[b]

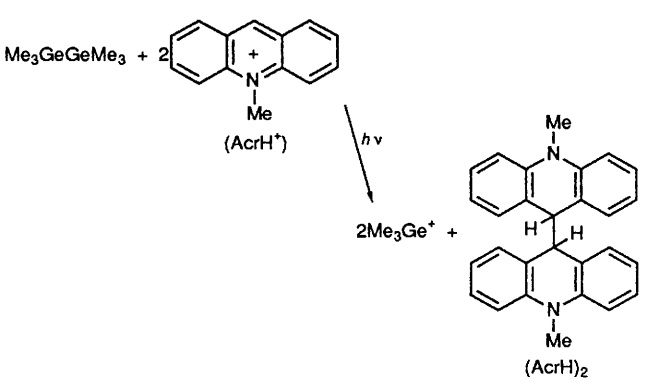
[a] *Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*
[b] *Department of Chemistry, Faculty of Sciences, Gakushuin University, Mejiro, Tokyo 171, Japan*

Efficient one-electron reduction of the 10-methylacridinium ion, with group 14 dimetallic compounds ($Me_3MM'Me_3$; M, M′ = Sn, Ge, Si), is initiated by electron transfer to the singlet excited state of the 10-methylacridinium ion in acetonitrile with irradiation by visible light to yield 10,10′-dimethyl-9,9′-biacridine selectively.

One-electron reduction of cationic substrates such as pyridinium ions is usually made possible by electrochemical methods, or by electron transfer from one-electron reductants, followed by the dimerization of the resulting radicals to yield the corresponding dimers.[1,2] There was no report on the selective one-electron reduction of cationic substrates by two-electron reductants until we reported recently that selective one-electron reduction of a cationic substrate, 10-methylacridinium ion ($AcrH^+$) occurs thermally by group 14 dimetallic compounds containing Sn (*e.g.* $Me_3SnSnMe_3$, $Me_3SnSiMe_3$),[3] which are known to be good two-electron σ-donors.[4] However, the group 14 dimetallic compounds which do not contain Sn show no reactivity towards $AcrH^+$ thermally.[3] This study reports that the one-electron reduction of $AcrH^+$ occurs efficiently with various group 14 dimetallic compounds ($Me_3MM'Me_3$; M, M′ = Sn, Ge, Si), under the irradiation by visible light (λ > 360 nm), to yield the corresponding dimer, 10,10′-dimethyl-9,9′-biacridine $(AcrH)_2$.†

Irradiation of the absorption band ($\lambda_{max.}$ 417 nm) of $AcrH^+$ (4.0×10^{-2} mol dm^{-3}) in deaerated acetonitrile containing $Me_3GeGeMe_3$ (4.0×10^{-2} mol dm^{-3}), using a xenon lamp for 6 h results in the formation of the dimer, 10,10′-dimethyl-9,9′-biacridine and Me_3GeClO_4 (90% yield) (Scheme 1). The photo-induced one-electron reduction of $AcrH^+$ also occurs with other group 14 dimetallic compounds ($Me_3GeSiMe_3$, $Me_3SnSiMe_3$, $Me_3SnSnMe_3$), except for $Me_3SiSiMe_3$ which results in a photo-induced two-electron reduction of $AcrH^+$ to give 9,10-dihydro-9-trimethylsilyl-10-methylacridine AcrH($SiMe_3$).[5]

The dependence of the quantum yield ϕ, determined using a ferrioxolate actinometer[6] with 358 nm irradiation, on [$Me_3MM'Me_3$] is given by equation (1), where k_{obs} is the



Scheme 1

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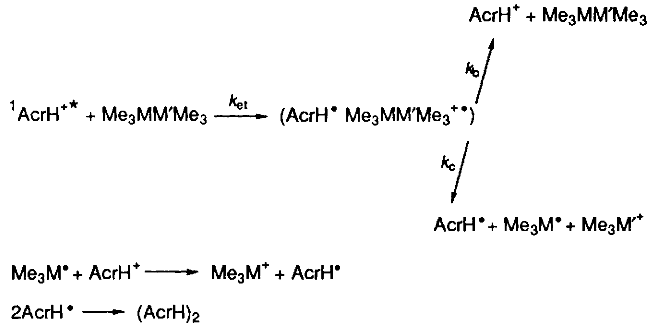
† Satisfactory elemental analysis was obtained for $(AcrH)_2$. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.06 (6H, s), 3.99 (2H, s), and 6.5—7.3 (16H, m); Me_3GeClO_4 (CD_3CN) δ 0.79 (9H, s).

Table 1. Limiting quantum yields (ϕ_∞), rate constants k_{obs}, k_q, k_{et}, (dm^3 mol^{-1} s^{-1}) one-electron oxidation potentials (E^0_{ox} *vs.* s.c.e.) of $Me_3MM'Me_3$, and the estimated ratio of the rate constants, $k_c/(k_c + k_b)$, for the photo-induced reduction of $AcrH^+$ by $Me_3MM'Me_3$.

$Me_3MM'Me_3$	ϕ_∞	E^0_{ox}/V[a]	k_{obs}	k_q	k_{et}[b]	$k_c/(k_c + k_b)$[c]
$Me_3SiSiMe_3$	0.038	0.92	7.1×10^9	7.1×10^9	8.7×10^9	0.042
$Me_3GeSiMe_3$	0.043	0.88	8.7×10^9	9.1×10^9	8.9×10^9	0.048
$Me_3GeGeMe_3$	0.039	0.84	9.0×10^9	9.3×10^9	9.2×10^9	0.057
$Me_3SnSiMe_3$	0.11	0.82	9.6×10^9	9.8×10^9	9.3×10^9	0.062
$Me_3SnSnMe_3$	0.13	0.68	1.2×10^{10}	1.2×10^{10}	9.6×10^9	0.13

[a] The E^0_{ox} values have been determined bv the analyses of cyclic voltammograms according to the method reported previously.[8,12] [b] Calculated by applying the Marcus theory;[9] the effect of diffusion on the k_{et} values is taken into account by using the equation $k_{et} = k_{diff}/[1 + 0.25 \exp(\Delta G^\ddagger_{et}/RT)]$,[10] where k_{diff} is taken as 1.2×10^{10} dm^3 mol^{-1} s^{-1}. [c] The k_b values are also calculated by applying the Marcus theory, see text.



Scheme 2

quenching rate constant of the excited state of $AcrH^+$ in the photoreduction of $AcrH^+$ and τ is the lifetime of the singlet excited state (τ 31 ns).[7,8] From the linear plots of ϕ^{-1} *vs.* $[Me_3MM'Me_3]^{-1}$, the ϕ_∞ and k_{obs} values are obtained which are listed in Table 1, together with the one-electron oxidation potentials of $Me_3MM'Me_3$ (E^0_{ox}).[3]

The fluorescence of $AcrH^+$ ($\lambda_{max.}$ 490 nm) is quenched by $Me_3MM'Me_3$ in MeCN at 298 K. The quenching rate constants k_q determined from the slopes of the Stern–Volmer plots, and the lifetime of the singlet excited state $^1AcrH^{+*}$ (τ 31 ns)[7,8] are also listed in Table 1, where the k_{obs} values agree well with the corresponding k_q values and also the calculated rate constants k_{et} of electron transfer from $Me_3MM'Me_3$ to $^1AcrH^{+*}$. The k_{et} values were calculated from the E^0_{ox} values, the one-electron reduction potential of $^1AcrH^{+*}$ [E^0_{red} 2.3 V *vs.* standard calomel electrode (s.c.e.)][8] and the reorganization energy (λ 38 kcal mol^{-1})[3] by using Marcus theory (Table 1).[9] Although such agreements, with values being close to the diffusion limit, are expected for highly exergonic electron-transfer reactions, the agreement suggests that the photo-induced one-electron reduction is initiated by electron transfer from $Me_3MM'Me_3$ to the singlet excited state $^1AcrH^{+*}$ as shown in Scheme 2. Since the one-electron oxidation of $Me_3MM'Me_3$ is known to result in the facile cleavage of metal–metal bonds,[11] electron transfer may yield the metal-centred radical $Me_3M^\bullet$ which has strong reducing ability. Another $AcrH^+$ molecule may be reduced by $Me_3M^\bullet$ to produce $AcrH^\bullet$ which dimerizes to yield the one-electron reduced product $(AcrH)_2$, [with $Me_3SiSiMe_3$ the radical coupling of $Me_3Si^\bullet$ and $AcrH^\bullet$ may occur to give $AcrH(SiMe_3)$ because of the lower reducing ability of $Me_3Si^\bullet$ compared with $Me_3Sn^\bullet$ and $Me_3Ge^\bullet$].[5] According to Scheme 2, the limiting quantum yield (ϕ_∞) may be determined by the competition between the back electron transfer from $AcrH^\bullet$ to $Me_3MM'Me_3^{+\bullet}$ (k_b) and the cleavage of metal–metal bonds of $Me_3MM'Me_3^{+\bullet}$ (k_c) as given by equation (2). The k_b values can also be calculated from the E^0_{ox} values, the one-electron reduction potential of $AcrH^+$ (E^0_{red} −0.43 V),[12] and the λ values by using Marcus theory. The $k_c/(k_c + k_b)$ values may then be estimated from the k_b values by using equation (2) in which the k_c values are assumed to be the same (1.6×10^{11} s^{-1}). The $k_c/(k_c + k_b)$ values agree reasonably well with the observed variation of ϕ_∞ values depending on $Me_3MM'Me_3$ (Table 1), demonstrating the validity of Scheme 1.

$$\phi^{-1} = \phi_\infty^{-1}\{[1 + (k_{obs}\,\tau\,[Me_3MM'Me_3])^{-1}\} \qquad (1)$$

$$\phi_\infty = k_c/(k_c + k_b) \qquad (2)$$

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