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Large Reorganization Energies Associated with Electron-Transfer Reactions of Permethylated Catenates of Group 4B Elements

Shunichi FUKUZUMI,* Toshiaki KITANO, and Kunio MOCHIDA[†]
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565
[†]Department of Chemistry, Faculty of Sciences, Gakushuin
University, Mejiro, Tokyo 171

Large reorganization energies (38±5 kcal mol^{-1}) are found to be required for electron-transfer reactions of permethylated catenates of group 4B elements. With such large reorganization energies the standard oxidation potentials of permethylated catenates of group 4B elements in acetonitrile are about 1 V lower than the corresponding peak potentials observed in the electrochemical oxidation.

The oxidative cleavage of the metal-metal bond of permethylated catenates of group 4B elements especially polysilanes has recently received considerable interest since they can act as electron-rich donor molecules as a consequence of their high-lying metal-metal σ bonding orbitals, which may be originated from the overlap of higher energy (3s, 3p) atomic orbitals than the corresponding carbon-based systems (2s, 2p) as well as σ-bond conjugation effects.[1,2] The electron-rich character of permethylated catenates of group 4B elements is also evident in many examples of the photoinduced electron-transfer reactions with electron acceptors.[3,4] However, no fundamental characters of permethylated catenates of group 4B elements in the electron-transfer reactions in solutions such as reorganization energies or the standard one-electron oxidation potentials have so far been reported. As such, highly positive oxidation peak potentials of group 4B dimetals (e.g., E^{p}_{ox} = 1.88 V vs. SCE for $Me_3SiSiMe_3$)[5] have been used in evaluating the Gibbs energy change of the electron transfer reactions,[4] although such highly positive values appear to contradict the electron-rich character.

We report herein that the large reorganization energies (λ = 38±5 kcal mol^{-1}) are required for electron-transfer reactions of various permethylated catenates of group 4B elements and that the actual one-electron oxidation potentials in acetonitrile are by about 1 V lower than the observed peak potentials.

The permethylated catenates of group 4B elements used in this study are $Me_3SiSiMe_3$, $Me(SiMe_2)_3Me$, $Me_3GeSiMe_3$, $Me_3SnSiMe_3$, $Me_3GeGeMe_3$, $Me_3SnGeMe_3$, and $Me_3SnSnMe_3$. The cyclic voltammograms of the group 4B organometallic compounds are characterized by well-defined anodic waves, but no cathodic waves were observed on the reverse scan, even at high scan rates.$^{5,6)}$ The irreversible behavior suggests that the one-electron oxidized species are unstable and the follow-up chemical reactions are fast on the time scale of the CV measurements. The anodic peak potentials E^{p}_{ox} and the width of the wave $E^{p}_{ox} - E^{p/2}_{ox}$ vary depending on the sweep rates. From the dependence of E^{p}_{ox} and $E^{p}_{ox} - E^{p/2}_{ox}$ on the sweep rate are determined the reorganization energies λ as well as the one-electron oxidation potentials E^{0}_{ox} of the group 4B organometallic compounds according to the method reported previously.$^{7)}$ The E^{0}_{ox} and λ values are listed in Table 1, together with the ionization potentials IP.$^{8)}$ The E^{0}_{ox} value increases in the order Si-Si-Si < Sn-Sn < Sn-Ge < Sn-Si < Ge-Ge < Ge-Si < Si-Si, in agreement with the IP value (Table 1). All the E^{0}_{ox} values are by about 1 V lower than the observed peak potentials reported previously.$^{5)}$ In contrast with the small reorganization energies of most organic compounds ($\lambda <$ 10 kcal mol^{-1}),$^{9)}$ the λ values of group 4B organometallic compounds are unusually large (31-46 kcal mol^{-1}). Such large reorganization energies may be ascribed to the large configurational changes associated with the one-electron oxidation as demonstrated by the ESR spectra of radical cations of

Table 1. The Ionization Potentials (IP), Standard One-Electron Oxidation Potentials (E^{0}_{ox}), and Reorganization Energies (λ) of Permethylated Catenates of Group 4B Elements

Group 4B compound No.		$IP^{a)}$/eV	E^{0}_{ox} vs. SCE/V	λ/kcal mol^{-1}
1	$Me_3SiSiMe_3$	8.68	0.92	40
2	$Me(SiMe)_3Me$	8.19	0.55	32
3	$Me_3GeSiMe_3$	8.62	0.88	38
4	$Me_3SnSiMe_3$	8.39	0.82	35
5	$Me_3GeGeMe_3$	8.60	0.84	46
6	$Me_3SnGeMe_3$	8.36	0.76	40
7	$Me_3SnSnMe_3$	8.20	0.68	31

a) Ref. 8.

group 4B dimetals in which each metal center becomes nearly planar.[10] This may be the reason why the large overpotentials (about 1V) are required to observe the current peaks (E^{p}_{ox}) in the electrochemical oxidation.

As electron-rich molecules permethylated catenates of group 4B elements can quench the singlet excited states of various organic electron acceptors by photoinduced electron transfer. A number of rate constants (k_{et}) of photoinduced electron-transfer reactions from the group 4B organometallic compounds to the singlet excited states of organic electron acceptors (pyrene, naphthalene, 9,10-dicyanoanthracene, and 10-methylacridinium ion) are determined by the fluorescence quenching in MeCN at 298 K. The log k_{et} values are plotted against the Gibbs energy change (ΔG^{0}_{et}) of the electron transfer from the group 4B organometallic compounds to electron acceptors in Fig. 1, where the ΔG^{0}_{et} values are obtained from the one-electron oxidation potentials (E^{0}_{ox}) in Table 1 and the one-electron reduction potentials of the singlet excited states of acceptors.[7,11] According to the Marcus theory,[12] the activation Gibbs energy of electron transfer ($\Delta G^{\ddagger}_{et}$) is calculated by Eq. 1, where

$$\Delta G^{\ddagger}_{et} = (\lambda/4)[1 + (\Delta G^{0}_{et}/\lambda)]^{2} \qquad (1)$$

$\Delta G^{0}_{et} = F(E^{0}_{ox} - E^{0}_{red})$ and F is the Faraday constant. Then the electron-transfer rate constant k_{et} is obtained by Eq. 2,

$$\Delta G^{\ddagger}_{et} = (RT/F)\ln[Z(k_{et}{}^{-1} - k_{diff}{}^{-1})] \qquad (2)$$

where Z (1×10^{11} dm^{3} mol^{-1} s^{-1}) and k_{diff} (2.0×10^{10} dm^{3} mol^{-1} s^{-1}) are the collision frequency and the diffusion rate constant in MeCN, respectively.[12] Thus, the k_{et} values can be calculated from the E^{0}_{ox} and λ values in Table 1 by using Eqs. 1 and 2.[13] The

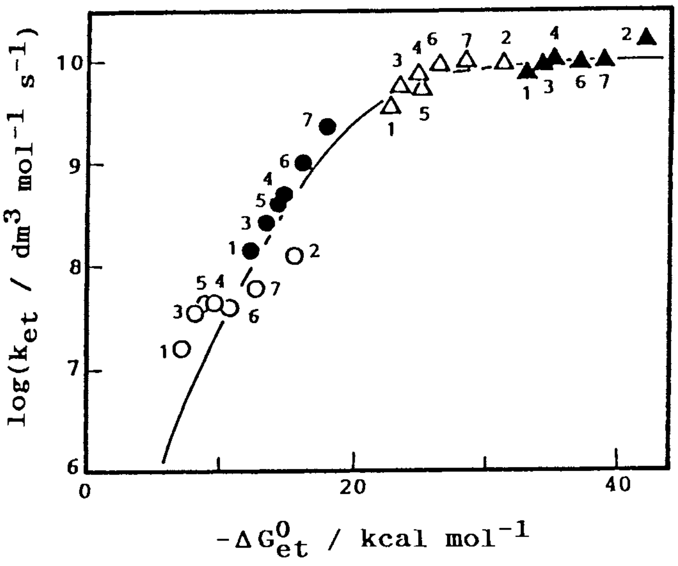

Fig. 1. Dependence of log k_{et} on ΔG^{0}_{et} for photoinduced electron transfer reactions from permethylated catenates of group 4B elements to pyrene (○), naphthalene (●), 9,10-dicyanoanthracene (△), and 10-methylacridinium ion (▲) in MeCN at 298 K. Numbers refer to the group 4B organometallic compounds in Table 1. The solid line shows the calculated dependence by the Marcus theory, see text.

calculated dependence of log k_{et} on ΔG^0_{et} shown by the solid line in Fig. 1 agrees well with experimental results for the photoinduced electron-transfer reactions of group 4B organometallic compounds, demonstrating clearly the validity of the E^0_{ox} and λ values in Table 1.

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13) The average λ value (38 ± 5 kcal mol^{-1}) in Table 1 is used for the calculation, by assuming the λ value in the electrochemical oxidation is the same as that in the photoinduced electron-transfer reactions.

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