

Photoelectron-transfer Reactions of Flavin Analogues with Tetra-alkyltin Compounds

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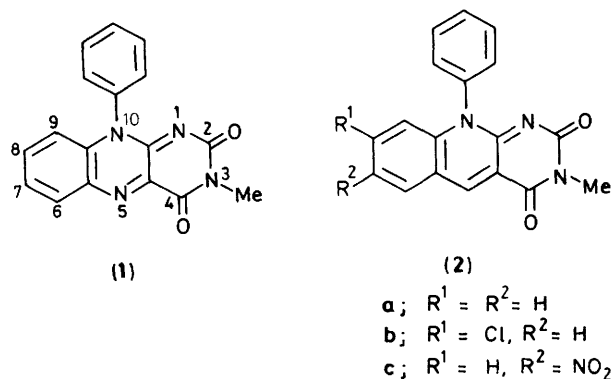
The fluorescence of flavin analogues (3-methyl-10-phenylisoalloxazine and 3-methyl-10-phenyl-5-deazaalloxazines) in the absence and presence of Mg^{2+} ion in acetonitrile was quenched by the electron-transfer reactions with tetra-alkyltin compounds. The quenching rate constants as well as the rate constants for electron-transfer reactions of the tetra-alkyltin compounds with iron(III) complexes $[Fe(N-N)_3]^{3+}$ ($N-N = 2,2'$ -bipyridine and various substituted 1,10-phenanthrolines) agree with those calculated by using the Marcus theory for outer-sphere electron-transfer reactions over a wide spread of values of the Gibbs energy change from the highly exothermic to the endothermic region. The intrinsic barrier λ for the electron-transfer reactions of tetra-alkyltin compounds is found to be significantly large, *i.e.*, $\lambda = 170 \text{ kJ mol}^{-1}$, compared with those of organic compounds (typically, $\lambda = 40 \text{ kJ mol}^{-1}$). A flavin analogue (3-methyl-10-phenylisoalloxazine) catalyses the photo-oxidation of tetra-alkyltin compounds by oxygen in the presence of Mg^{2+} ion in acetonitrile, which proceeds *via* the photoelectron-transfer from tetra-alkyltin compounds to the excited state of the flavin.

Photoelectron-transfer reactions are receiving increased attention in the field of inorganic¹ as well as organic chemistry.^{2,3} The basic concept and its application have been extended not only to the field of biomimetic chemistry but also to that of biochemistry.⁴ In fact, photoelectron-transfer reactions of flavin, which is a principal coenzyme of biochemical redox reactions, with various organic reductants have been extensively studied.⁴⁻⁷ In contrast, relatively little is known of photoelectron-transfer reactions of organometallic compounds, especially alkylmetals, despite the fact that many alkylmetals are known to be good electron donors.⁸

In this paper, we report photoelectron-transfer reactions of flavin analogues [3-methyl-10-phenylisoalloxazine (1), 3-methyl-10-phenyl-5-deazaalloxazine (2a), 3-methyl-8-chloro-10-phenyl-5-deazaalloxazine (2b), 3-methyl-7-nitro-10-phenyl-5-deazaalloxazine (2c)] with tetra-alkyltin compounds R_4Sn ($R = \text{Me, Et, Pr}^i, \text{Bu}^n$) in the absence and presence of Mg^{2+} ion in acetonitrile (MeCN). The redox potentials of R_4Sn can be tuned by changing the alkyl group,⁹ and those of the singlet-excited states of flavin analogues are changed by the complex formation with Mg^{2+} ion in MeCN.⁷ Since an outer-sphere electron-transfer mechanism has well been established for electron-transfer reactions from R_4Sn to iron(III) complexes $[Fe(N-N)_3]^{3+}$ ($N-N = 2,2'$ -bipyridine and various substituted 1,10-phenanthrolines),⁹ the present study provides an opportunity to establish the functional dependence of the rate constants for electron-transfer reactions of R_4Sn over a wide range of the Gibbs energy change of electron transfer ranging from the highly exothermic photoelectron-transfer reactions to the endothermic thermal electron-transfer reactions. Then, the applicability of the Marcus theory, which is known to be particularly useful for predicting electron-transfer rates when the Gibbs energy change of electron-transfer is nearly zero,¹⁰ will be tested for the electron-transfer reactions of R_4Sn over a wide spread of values of the Gibbs energy change of electron transfer. We report also the photo-oxidation of R_4Sn by oxygen, catalysed by a flavin analogue (1)- Mg^{2+} complex in MeCN, which is initiated by photoelectron transfer from R_4Sn to the excited state of (1).

Experimental

Materials.—Preparations of flavin analogues (1) and (2a–c) were described elsewhere.^{7,11} A series of tetra-alkyltin



compounds was prepared according to the standard procedures.^{9,12} Anhydrous metal perchlorates $Mg(ClO_4)_2$ and $NaClO_4$ were obtained commercially and dried before use. Potassium ferrioxalate used as an actinometer was prepared according to the literature,¹³ and purified by recrystallization from hot water. Acetonitrile used as a solvent was purified and dried by the standard procedure,¹⁴ and stored on calcium hydride under nitrogen.

Fluorescence-quenching Experiments.—Fluorescence measurements were carried out on a Hitachi 650-10S fluorescence spectrophotometer. Quenching experiments of the flavin analogue fluorescence in the absence and presence of $Mg(ClO_4)_2$ in MeCN were carried out by using tetra-alkyltin compounds as quenchers. Relative fluorescence intensities of a flavin analogue at the emission maximum [λ_{max} , for (1) 506, for (2a–c) 451 nm in the absence of $Mg(ClO_4)_2$; λ_{max} , for (1) 493, for (2a) 439, for (2b) 434, for (2c) 443 nm in the presence of $0.10 \text{ mol dm}^{-3} Mg(ClO_4)_2$] were measured for MeCN solutions containing a flavin analogue and a quencher at a variety of concentrations. There was no change in the shape but the intensity of the fluorescence spectrum changed on addition of tetra-alkyltin compounds. The Stern–Volmer relationship was obtained between the ratio of the fluorescence intensity in the absence and presence of a quencher I_f^0/I_f and the quencher concentration $[R_4Sn]$ as expressed by equation (1), where k_q is the quenching

$$I_f^0/I_f = 1 + k_q\tau[R_4Sn] \quad (1)$$

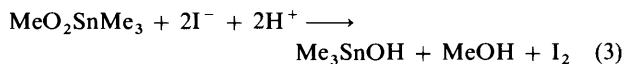
rate constant and τ is the fluorescence lifetime of flavin analogues [τ for (1) 2.4, for (2a) 1.7, for (2b) 1.8, for (2c) 0.38 ns in the absence of $Mg(ClO_4)_2$; for (1) 1.7, for (2a) 1.6, for (2b) 1.0, for (2c) 0.19 ns in the presence of $0.10 \text{ mol dm}^{-3} Mg(ClO_4)_2$].⁷

Determination of Redox Potentials of the Singlet-excited States of Flavin Analogues.—The redox potential of (1) was determined by the cyclic voltammetry measurements using a Hokuto Denko model HA-301 potentiostat–galvanostat at 298 K. The electrochemical reduction of (1) in MeCN with a platinum microelectrode under deaerated conditions was reversible and the redox potential of the couple (1)/(1⁻) was determined as 0.76 V versus a standard NaCl calomel reference electrode (s.c.e.). The redox potential of the singlet-excited state of (1) $E^0(I^*/I^{*-})$ was determined as the sum of that of the ground state $E^0(I)/I^{*-}$ and the excitation energy $\Delta E_{0,0}$ [equation (2)], where the $\Delta E_{0,0}$ value was obtained as 2.64 eV

$$E^0(I^*/I^{*-}) = E^0(I)/I^{*-} + \Delta E_{0,0} \quad (2)$$

(1 eV = 1.60×10^{-19} J) from the frequencies of the absorption and the fluorescence maxima of (1). Although the electrochemical reduction of flavin analogues other than (1) was irreversible, their $E^0(I^*/I^{*-})$ values were determined based on the value of (1) since the relative values of $E^0(I^*/I^{*-})$ referenced to (1) in the absence and presence of $0.10 \text{ mol dm}^{-3} Mg(ClO_4)_2$ have been previously reported.⁷

Photo-oxidation of Tetra-alkyltin Compounds.—The photo-oxidation of Me_4Sn by oxygen, catalysed by a (1)– Mg^{2+} complex, was monitored by using a Japan Electron Optics JNM-PS-100 ¹H n.m.r. spectrometer. Typically, Me_4Sn ($6.2 \times 10^{-3} \text{ cm}^3$) was added to an n.m.r. tube which contained a CD_3CN solution (0.50 cm^3) of a flavin analogue (1) ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) and $Mg(ClO_4)_2$ (0.10 mol dm^{-3}). After the reactant solution was saturated with oxygen, it was irradiated with the visible light from an Ushio model U1-501 Xenon lamp through a Toshiba filter C-39A transmitting light of $350 \text{ nm} < \lambda < 470 \text{ nm}$. The relevant ¹H n.m.r. data are δ 0.06 (12 H, s) for Me_4Sn and 0.53 (9 H, s) and 3.77 (3 H, s) for the oxidation product MeO_2SnMe_3 . The oxidation product was quantitatively converted into Me_3SnOH and $MeOH$ by treatment with an aqueous solution of NaI [equation (3)]. The products of photo-oxidation of Pr^i_4Sn were analysed also by g.l.c.



A standard actinometer (potassium ferrioxalate)¹³ was used for the quantum-yield determinations on the photo-oxidation of R_4Sn by oxygen, catalysed by a (1)– Mg^{2+} complex in MeCN. The actinometry experiments were carried out under conditions such that both an actinometer and a (1)– Mg^{2+} complex absorb essentially all the incident light (>95%) through the filter ($350 \text{ nm} < \lambda < 470 \text{ nm}$). The quantum yields of the photo-oxidation of Me_4Sn were determined from the rate of formation of MeO_2SnMe_3 measured by the iodometry according to equation (3), and those of Pr^i_4Sn were determined from the rate of formation of acetone and isopropyl alcohol measured by g.l.c.

Results and Discussion

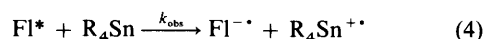
Fluorescence Quenching of Flavin Analogues with Tetra-alkyltin Compounds.—The fluorescence of a flavin analogue may be quenched by electron-transfer reactions with tetra-

Table 1. Rate constants k_{obs} for the fluorescence quenching of flavin analogues (1) and (2a–c) by R_4Sn in the absence and presence of $0.10 \text{ mol dm}^{-3} Mg(ClO_4)_2$ and the redox potentials of the singlet-excited states of the flavin analogues $E^0(I^*/I^{*-})$ (versus s.c.e.) in MeCN

Entry	Flavin	$E^0(I^*/I^{*-})/V$	$\log(k_{obs}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ of R_4Sn			
			R = Me	R = Et	R = Pr ⁱ	R = Bu ⁿ
1	(1)	1.96	<i>b</i>	9.31	10.03	9.49
2	(1)– Mg^{2+} ^a	2.28	8.54	9.73	10.12	9.93
3	(2a)	1.77	<i>b</i>	8.69	10.04	8.75
4	(2a)– Mg^{2+} ^a	2.10	8.19	9.50	10.10	9.50
5	(2b)	1.88	<i>b</i>	8.81	10.15	9.30
6	(2b)– Mg^{2+} ^a	2.22	<i>b</i>	9.77	10.28	9.83
7	(2c)	1.95	<i>b</i>	9.47	10.02	9.31
8	(2c)– Mg^{2+} ^a	2.27	8.85	10.00	10.56	10.10

^a In the presence of $0.10 \text{ mol dm}^{-3} Mg(ClO_4)_2$. ^b Too small to be determined accurately.

alkyltin compounds R_4Sn (R = Me, Et, Buⁿ, Prⁱ) in the absence and presence of $Mg(ClO_4)_2$ in MeCN [equation (4)] since

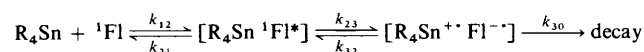


energy transfer from Fl^* to R_4Sn is unlikely to occur because of the much higher excited states of R_4Sn than those of Fl . The quenching rate constants k_{obs} obtained from the slopes of the Stern–Volmer plots [equation (1)] and the fluorescence lifetimes are listed in Table 1, which also shows the redox potentials of the singlet-excited states of flavin analogues $E^0(I^*/I^{*-})$ in the absence and presence of $0.10 \text{ mol dm}^{-3} Mg(ClO_4)_2$ in MeCN (see Experimental section). In the presence of $0.10 \text{ mol dm}^{-3} Mg(ClO_4)_2$, most flavin molecules are known to form the 1:1 complex with Mg^{2+} ion [equation (5)].^{7,15} Thus, the redox potentials of the singlet-excited states



of flavin analogues are shifted in the positive direction (*ca.* +0.2 V) by the complex formation with Mg^{2+} ion (Table 1). In fact, the k_{obs} values for the electron-transfer quenching of Fl^* with Me_4Sn , Et_4Sn , and Bu^n_4Sn increased on increasing the Mg^{2+} concentration, and attained a constant value at high concentrations of Mg^{2+} ion (*e.g.*, 0.10 mol dm^{-3}) in each tetra-alkyltin, while the k_{obs} values with the strongest electron donor among R_4Sn used in this study, *i.e.* Pr^i_4Sn , are close to the diffusion rate constant $2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$,¹² as shown in Table 1. Such an increase of the k_{obs} value in the presence of Mg^{2+} ion cannot be attributed to a salt effect since the addition of $0.10 \text{ mol dm}^{-3} NaClO_4$ or $NBu^n_4ClO_4$ to the Fl – R_4Sn system has caused essentially no effect on the quenching rate constant.

Application of the Marcus Theory to Electron-transfer Reactions of Tetra-alkyltin Compounds.—By applying the general scheme for the fluorescence quenching by electron transfer in MeCN to the present system (Scheme 1),^{16,17} the



Scheme 1.

observed quenching rate constant k_{obs} [equation (4)] may be expressed by equation (6), where k_{30} comprises all possible

$$k_{obs} = \frac{k_{12}}{1 + \frac{k_{21}}{k_{30}} \left(\frac{k_{30}}{k_{23}} + \frac{k_{32}}{k_{23}} \right)} \quad (6)$$

modes by which the radical ion pair disappears, in particular *via* the back electron-transfer to the triplet and/or ground states of FI as well as the rapid fragmentation of $R_4Sn^{+\cdot}$ in equation (7),⁹



being approximately equal to the frequency factor. Under such conditions, equation (6) can be rewritten as (8), where ΔG_{23}^\ddagger

$$k_{\text{obs}} = \frac{2.0 \times 10^{10}}{1 + 0.25[\exp(\Delta G_{23}^\ddagger/RT) + \exp(\Delta G_{23}/RT)]} \quad (8)$$

and ΔG_{23} are the activation Gibbs energy and the Gibbs energy change of the actual electron-transfer process, respectively. A theoretical basis for the outer-sphere electron-transfer process is well provided by the Marcus theory which predicts the dependence of ΔG_{23}^\ddagger on ΔG_{23} as expressed by equation (9),¹⁰

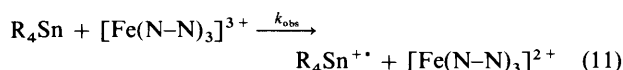
$$\Delta G_{23}^\ddagger = \frac{\lambda}{4} \left[1 + \frac{\Delta G_{23}}{\lambda} \right]^2 \quad (9)$$

where λ is the reorganization energy of the electron transfer. Thus, the k_{obs} value can be theoretically calculated as a function of ΔG_{23} by using equations (8) and (9).

On the other hand, ΔG_{23} is obtained from the difference in the redox potentials between R_4Sn and FI^* by equation (10), where w_p is the work term required to bring the products together to the mean separation in the activated complex, and the corresponding work term for the neutral reactants w_r is neglected. Then, the logarithms of the observed rate constants in Table 1 are plotted as a function of ΔG_{23} which is obtained from the values of $E^0(R_4Sn^{+\cdot}/R_4Sn)$ ⁹ and $E^0(FI^*/FI^{\cdot-})$ by using equation (10), taking into account a work term w_p for the

$$\Delta G_{23} = F[E^0(R_4Sn^{+\cdot}/R_4Sn) - E^0(FI^*/FI^{\cdot-})] + w_p \quad (10)$$

$R_4Sn^{+\cdot}-FI^{\cdot-}$ system at -9.6 kJ mol^{-1} ,¹⁷ as shown in Figure 1. The $\log k_{\text{obs}}$ values for the thermal electron-transfer reactions of R_4Sn ($R = \text{Me, Et, Bu}^n, \text{Pr}^i$) and Et_4Pb with $[\text{Fe}(\text{N}-\text{N})_3]^{3+}$ ($\text{N}-\text{N} = 2,2'$ -bipyridine and various substituted 1,10-phenanthrolines) reported previously [equation (11)]⁹



are also plotted as a function of ΔG_{23} in Figure 1. Thus, the experimental dependence of $\log k_{\text{obs}}$ for the electron-transfer reactions of R_4Sn over a wide range of the Gibbs energy change of the electron transfer has been established in Figure 1, which covers the range from highly exothermic photoelectron-transfer to endothermic thermal electron-transfer reactions.

The theoretical rate constants for the electron-transfer reactions calculated by using equations (8) and (9) with the λ value of 170 kJ mol^{-1} are shown by the solid line in Figure 1, which agrees well with the experimental results. Such agreements demonstrate that the Marcus theory can well be applied for the highly exothermic as well as endothermic electron-transfer reactions with the large reorganization energy assuming that k_{30} is equal to the frequency factor, although the applicability of the Marcus theory is generally believed to decrease as the Gibbs energy change of electron transfer becomes largely negative or positive.¹⁸ The large λ value (170 kJ mol^{-1}) in the present case shows a marked contrast with a much smaller λ value (40 kJ mol^{-1}) for the photoelectron-transfer reactions of FI with benzene derivatives.⁷ Thus, the intrinsic barrier for the electron-transfer reactions of R_4Sn with the oxidants (oxidants FI^* and $[\text{Fe}(\text{N}-\text{N})_3]^{3+}$), which may be

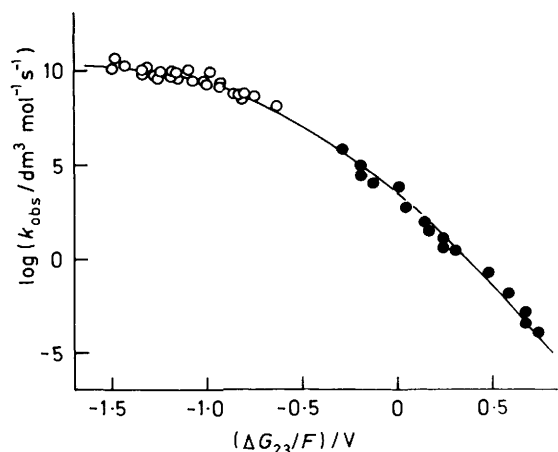


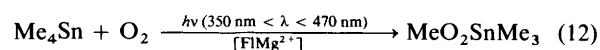
Figure 1. Plots of the logarithms of the observed rate constants $\log k_{\text{obs}}$ for the photoelectron-transfer reactions of R_4Sn with flavin analogues in the absence and presence of $0.10 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ ion (O) (Table 1) and for the electron-transfer reactions of R_4Sn ($R = \text{Me, Et, Bu}^n, \text{Pr}^i$) and Et_4Pb with $[\text{Fe}(\text{N}-\text{N})_3]^{3+}$ (●) in MeCN at 298 K versus the Gibbs energy change of the electron transfer ($\Delta G_{23}/F$); the solid line shows the calculated dependence of $\log k_{\text{obs}}$ on $\Delta G_{23}/F$ based on the Marcus theory, see text

Table 2. Yields of $\text{MeO}_2\text{SnMe}_3$ based on (1) ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$) in the photo-oxidation of Me_4Sn (0.10 mol dm^{-3}) by oxygen, catalysed by (1) in the presence of $\text{Mg}(\text{ClO}_4)_2$ (0.10 mol dm^{-3}) in CD_3CN

t/h	Yield (%)
2	210
3	340
4	450
15	1 000

average for the reorganization energies for the self-exchange of the $\text{Ox}-\text{Ox}^{\cdot-}$ and $R_4Sn-R_4Sn^{+\cdot}$ systems, comprises mainly the latter system, where the contribution of the bond change in the inner co-ordination shell ($\text{Sn}-\text{R}$ bond) upon electron transfer may be important since the reorganization energy of the solvent shells of R_4Sn has been estimated as being much smaller ($50-84 \text{ kJ mol}^{-1}$)² than the observed λ value (170 kJ mol^{-1}). Similar large reorganization energies for the electrochemical oxidation of a series of organocobaloximes have recently been reported, showing that the large λ value reflects both electronic effects and steric distortions on the axial $\text{Co}-\text{C}$ bond, where bigger changes in the transition from the reacting particle to the activation state are localized.¹⁹

Flavin-catalysed Photo-oxidation of Tetra-alkyltin Compounds.—Irradiation of an oxygen-saturated CD_3CN solution containing a flavin analogue (1) ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$), Me_4Sn (0.10 mol dm^{-3}), and $\text{Mg}(\text{ClO}_4)_2$ (0.10 mol dm^{-3}) with visible light of $350 \text{ nm} < \lambda < 470 \text{ nm}$ results in the formation of $\text{MeO}_2\text{SnMe}_3$ (see Experimental section) [equation (12)]. Yields



of $\text{MeO}_2\text{SnMe}_3$ based on the initial amount of (1) reach 1 000% in 15 h (Table 2), demonstrating that (1) in the presence of Mg^{2+} ion acts as a photocatalyst in the photo-oxidation of Me_4Sn . It has been confirmed that neither thermal oxidation of Me_4Sn by oxygen nor photo-oxidation of Me_4Sn in the absence of (1) occurs. In the flavin-catalysed photo-oxidation of Me_4Sn , Mg^{2+} ion plays an essential role, since in the absence of Mg^{2+}

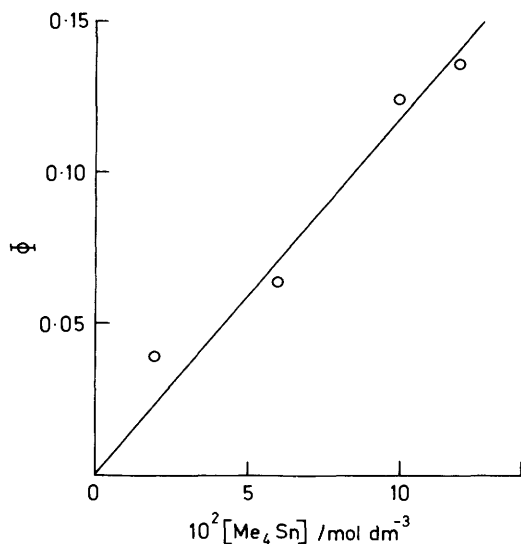


Figure 2. Plot of quantum yields Φ for the photo-oxidation of Me_4Sn by oxygen, catalysed by (1)- Mg^{2+} ($2.2 \times 10^{-4} \text{ mol dm}^{-3}$) in MeCN at 298 K versus the concentration of Me_4Sn

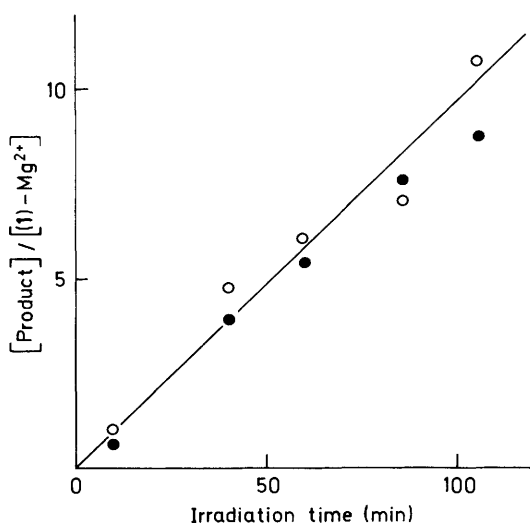


Figure 3. Plots of molar ratios of products [$\text{Me}_2\text{C}=\text{O}$ (○) and Pr^iOH (●)] to the initial amount of (1)- Mg^{2+} ($2.2 \times 10^{-4} \text{ mol dm}^{-3}$) versus irradiation time for the photo-oxidation of Pr^i_4Sn by oxygen, catalysed by (1)- Mg^{2+} in MeCN

ion, photo-oxidation has hardly been observed. The role of Mg^{2+} ion may not only be to increase the oxidizing ability of the excited state of (1) as indicated by the enhanced fluorescence quenching of Fl by R_4Sn in the presence of Mg^{2+} ion (Table 1), but also to stabilize (1) against irradiation of the visible light to prevent the photodegradation of (1) by forming the complex with Mg^{2+} ion [equation (5)]. In fact, the quantum yield of the photodegradation of (1)- Mg^{2+} complex (Φ_d 6.2×10^{-4}) is much smaller than that of a free flavin (1) (Φ_d 1.6×10^{-2}).⁷ The quantum yield for the photo-oxidation of Me_4Sn by oxygen, catalysed by a (1)- Mg^{2+} complex in MeCN, is proportional to the Me_4Sn concentration (Figure 2).

In contrast with the case of Me_4Sn , the photo-oxidation of Pr^i_4Sn by oxygen, catalysed by a (1)- Mg^{2+} complex, gives essentially no peroxy compound $\text{Pr}^i\text{O}_2\text{SnPr}^i_3$ but instead

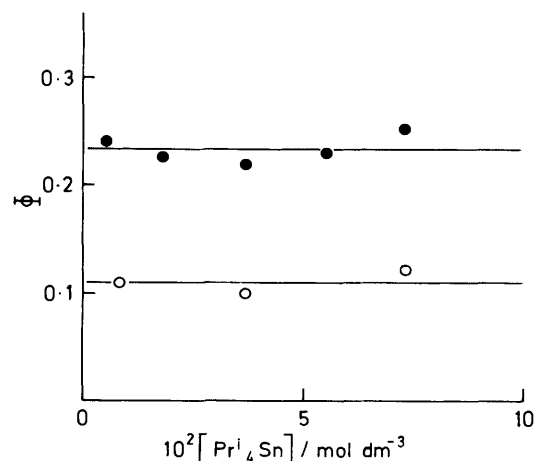
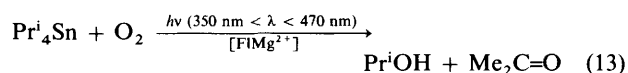


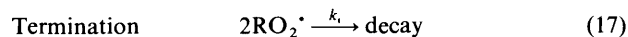
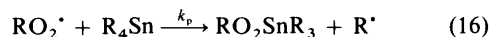
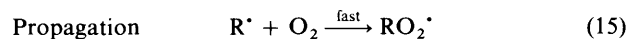
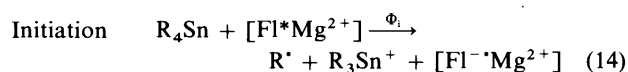
Figure 4. Plots of quantum yields Φ for the photochemical reaction of (1)- Mg^{2+} ($2.2 \times 10^{-4} \text{ mol dm}^{-3}$) with Pr^i_4Sn in the absence (●) and presence of oxygen (○) in MeCN at 298 K versus the concentration of Pr^i_4Sn

approximately equal amounts of isopropyl alcohol and acetone [equation (13)] as shown in Figure 3. In addition, the quantum



yield for photo-oxidation as well as the photochemical reaction of a (1)- Mg^{2+} complex with Pr^i_4Sn under a degassed condition is independent of the Pr^i_4Sn concentration (Figure 4).

The products of the photo-oxidation of R_4Sn [equation (12) and (13)] as well as the dependences of Φ on the R_4Sn concentration (Figures 2 and 4) can be explained by the radical chain mechanism (14)–(17), similar to that previously established for autoxidations of alkylborons²⁰ and alkylzirconocenes.²¹ In reaction (14) Φ_i is the quantum yield for the photoinitiation step



[equation (14)]. Since the one-electron oxidation of R_4Sn results in the facile fragmentation of $\text{R}_4\text{Sn}^{+\cdot}$ to yield R^\cdot [equation (7)],⁹ the autoxidation of R_4Sn may proceed by the radical chain reactions (15) and (16). The termination step of primary and secondary alkylperoxy radicals is known to give equal amounts of alcohol and ketone in reaction (17).²² By applying the steady-state approximation to the radical species involved in equations (14)–(17), the quantum yield for the photo-oxidation of R_4Sn Φ is given by equation (18), where

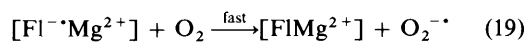
$$\Phi = \Phi_i + k_p(\Phi_i/2k_t\text{In})^{1/2}[\text{R}_4\text{Sn}] \quad (18)$$

In is the light intensity absorbed by a (1)- Mg^{2+} complex. In the case of Me_4Sn , the term for the chain-propagation step $k_p(\Phi_i/2k_t\text{In})^{1/2}[\text{Me}_4\text{Sn}]$ may be much larger than that for the photoinitiation step Φ_i in equation (18), and thereby Φ is proportional to $[\text{Me}_4\text{Sn}]$ whereas Φ_i is independent of $[\text{Me}_4\text{Sn}]$, as shown in Figure 2. Conversely, in the case of Pr^i_4Sn , the photoinitiation step becomes dominant with little contribution

from the chain-propagation step, to give mainly the termination products (isopropyl alcohol and acetone), and thus Φ which is equal to Φ_i is independent of $[\text{Pr}^i_4\text{Sn}]$ as shown in Figure 4. Such a difference between the photo-oxidation of Me_4Sn and that of Pr^i_4Sn may be ascribed to the more efficient photoinitiation in the case of Pr^i_4Sn than the case of Me_4Sn as predicted by the much faster fluorescence quenching of a $(1-\text{Mg}^{2+})$ complex by Pr^i_4Sn than by Me_4Sn (Table 1) as well as the higher reactivity of the primary alkylperoxyl radical (MeO_2^{\cdot}) than the secondary alkylperoxyl radical ($\text{Pr}^i\text{O}_2^{\cdot}$) in the propagation step (16).²²

The constant Φ_i value in the case of Pr^i_4Sn (Figure 4) suggests that the quenching process of the excited state $[\text{Fl}^*\text{Mg}^{2+}]$ by Pr^i_4Sn [equation (14)] is much faster than the other decay processes by the radiation and non-radiation pathways under the experimental conditions of Figure 4. Then, the minimum lifetime of the excited state involved in the photoinitiation step [equation (14)] can be estimated as $\tau \gg 10$ ns by using the relation $k_{\text{diff}}\tau[\text{R}_4\text{Sn}] \gg 1$, where the diffusion rate constant $k_{\text{diff}} = 2.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $[\text{Pr}^i_4\text{Sn}] \geq 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ (Figure 4). Since the fluorescence lifetime of $[(1^*)-\text{Mg}^{2+}]$ (τ 1.7 ns) is much shorter than the minimum lifetime of the reactive excited state, the triplet state of the flavin is the most plausible reactive species for the photoinitiation step (14) as in the case of most photochemical reactions of flavin analogues.²³

Since the photo-oxidation of Pr^i_4Sn which has no radical chain character proceeds in the presence of a catalytic amount of Fl (Figure 3), the photocatalyst may be regenerated by the fast oxidation of the reduced species $[\text{Fl}^-\text{Mg}^{2+}]$ by oxygen [equation (19)]. In fact, the second-order rate constant for the



reaction of $\text{Fl}^-\text{Mg}^{2+}$ with O_2 has been reported to be *ca.* $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.²⁴

In conclusion, R_4Sn can readily be oxidized by the photo-electron-transfer reactions with the excited states of flavin analogues, resulting in the facile fission of the Sn-R bond to give alkyl radical R^{\cdot} , competing well with the back electron-transfer processes. The resulting alkyl radical reacts with oxygen to yield alkylperoxyl radical which undergoes the autoxidation of R_4Sn by the radical chain mechanism or to yield alcohol and ketone by the bimolecular reaction of alkylperoxyl radicals, depending on the alkyl group of R_4Sn . In the electron-transfer reactions of R_4Sn , the large intrinsic barrier for the electron transfer (λ 170 kJ mol^{-1}) reflects the extensive changes of the metal-alkyl bond upon one-electron oxidation.

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