# Quantitative Evaluation of Lewis Acidity of Organotin Compounds and the Catalytic Reactivity in Electron Transfer

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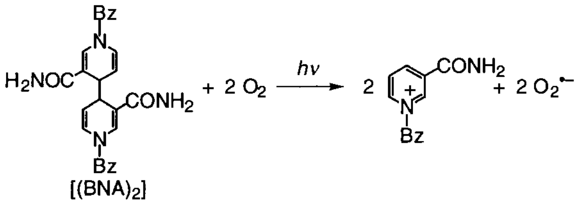
The *g*-values of ESR spectra of superoxide ($O_2^{\bullet-}$) complexes with various organotin compounds acting as Lewis acids were determined in acetonitrile at 143 K. The binding energies ($\Delta E$) in the complexes between organotins and $O_2^{\bullet-}$ have been evaluated from deviation of the $g_{zz}$-values from the free spin value. The $\Delta E$ values are well correlated with the catalytic reactivity of organotins as well as a series of metal ions acting as Lewis acids to promote electron transfer from cobalt(II) tetraphenylporphyrin to $O_2$, which would not occur in the absence of Lewis acids under otherwise the same experimental conditions.

Despite of their availability, organotin halides have seldom worked as Lewis acids in organic synthesis because of their weak acidity.[1] However, it has recently been shown that incorporation of pentafluorophenyl groups on tin makes it possible to catalyze a variety of nucleophilic reactions of silyl and stannyl substrates under mild conditions, thus allowing otherwise difficult-to-achieve differentiations between various carbonyls or between carbonyl and acetal.[2,3] Pentafluorophenyltin compounds such as $(C_6F_5)_2SnBr_2$ are unique and useful, since they are hydrolytically stable enough to be isolated by column chromatography or distillation in open air, in contrast to most of the conventional Lewis acids that are sufficiently acidic to promote synthetically useful reactions. Rare-earth metal ions are also known to act hydrolytically stable Lewis acids.[4] However, the Lewis acidity of pentafluorophenyltin compounds has yet to be evaluated quantitatively in comparison with metal ions acting as Lewis acids.[5]

We have recently reported that the $g_{zz}$-values of ESR spectra of superoxide ($O_2^{\bullet-}$)–metal ion ($M^{n+}$, n = 1, 2, 3) complexes are highly sensitive to the Lewis acidity of a variety of metal ions and that the binding energies readily derived from the $g_{zz}$-values provide the first quantitative experimental measure of Lewis acidity of $M^{n+}$ including rare-earth metal ions and that they are directly correlated with the promoting effects in electron transfer reduction of oxygen.[6]

We report herein the quantitative evaluation of the Lewis acidity of pentafluorophenyltin compounds as well as other organotin compounds derived from the $g_{zz}$-values of ESR spectra of $O_2^{\bullet-}$–organotin complexes. The present study provides an excellent opportunity to compare the Lewis acidity and the catalytic reactivity of organotin compounds quantitatively with a series of metal ions.

Superoxide ion is produced by the photoinduced reduction of $O_2$ by the dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] in acetonitrile (MeCN),[7] which can act as a unique two electron donor, as shown in eq 1.



(1)

When an oxygen-saturated MeCN solution containing $(BNA)_2$ ($1.0 \times 10^{-4}$ M, M = mol $dm^{-3}$) was irradiated with a high pressure mercury lamp, $O_2^{\bullet-}$ formed photochemically is detected by the ESR spectrum in frozen MeCN at 143 K. The ESR spectrum showed a typical anisotropic signal with $g_{//}$ = 2.090 and $g_{\perp}$ = 2.005.[8] The ESR spectra of $O_2^{\bullet-}$ produced in the presence of pentafluorophenyltin compounds were also measured at 143 K as shown in Figure 1 where the $g_{zz}$-values of $O_2^{\bullet-}$ in the presence of pentafluorophenyltin derivatives become significantly smaller than the value of free $O_2^{\bullet-}$ due to the complexation of pentafluorophenyltin derivatives with $O_2^{\bullet-}$.

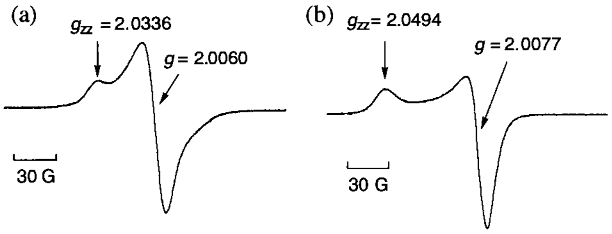


**Figure 1.** ESR spectra of (a) $O_2^{\bullet-}$–$(C_6F_5)_2SnBr_2$ and (b) $O_2^{\bullet-}$–$(C_6F_5)_4Sn$ in frozen MeCN at 143 K.

The *g*-tensor in particular $g_{zz}$-value gives valuable information concerning the binding strength between $O_2^{\bullet-}$ and organotins. The deviation of the $g_{zz}$-value from the free spin value ($g_e$ = 2.0023) is caused by the spin-orbit interaction as given by eq 2,[9] where $\lambda$ is the spin-orbit coupling constant of oxygen which is known as 0.014 eV,[10] and $\Delta E$ is the energy splitting of $\pi_g$ levels due to the complex formation between $O_2^{\bullet-}$ and organotins. Under the conditions that $\Delta E >> \lambda$, eq 2 is reduced to a simple relation, $g_{zz} = g_e + 2\lambda/\Delta E$. The $\Delta E$ values of $O_2^{\bullet-}$ complexes with a variety of organotins were determined from the deviation of the $g_{zz}$-values from the $g_e$-value.

$$g_{zz} = g_e + 2\sqrt{\frac{\lambda^2}{\lambda^2 + \Delta E^2}} \qquad (2)$$

Metal ions have been reported to promote electron transfer from (TPP)Co ($TPP^{2-}$ = dianion of tetraphenylporphyrin) to $O_2$, although no reaction between (TPP)Co and $O_2$ occurs in the absence of metal ions in MeCN.[6] Such promoting effects of metal ions in electron transfer reduction of $O_2$ have been ascribed to the binding of metal ions to $O_2^{\bullet-}$ produced in the electron transfer reactions.[6,11] An efficient electron transfer from (TPP)Co to $O_2$ also occurs in the presence of organotins such as $(C_6F_5)_2SnBr_2$ to yield $[(TPP)Co]^+$ and the $O_2^{\bullet-}$ complex (eq 3).

$$\mathrm{(TPP)Co} + O_2 + (C_6F_5)_2SnBr_2 \longrightarrow [\mathrm{(TPP)Co}]^+ + O_2^{\bullet-}\text{–}(C_6F_5)_2SnBr_2 \quad (3)$$

The electron transfer rates obeyed second-order kinetics, showing a first-order dependence on each concentration of (TPP)Co and $O_2$. The observed second-order rate constant ($k_{obs}$) for the organotin-promoted electron transfer increases linearly with increasing the organotin concentration. The catalytic rate constant of Lewis acid-promoted electron transfer ($k_{et}$) was determined from the slope of the linear plot of $k_{obs}$ vs [Sn], where [Sn] is the concentration of organotin.

There is a striking single linear correlation between log $k_{et}$ and $\Delta E$ of the $O_2^{\bullet-}$ complexes with organotins as well as metal ions (triflate or perchlorate salts) derived from the $g_{zz}$-values as shown in Figure 2. The remarkable correlation spans a range of almost $10^7$ in the rate constant. The slope of the linear correlation between log $k_{et}$ and $\Delta E$ is obtained as 14.0 which is close to the value of $1/(2.3kT)$ (=16.9, where $k$ is the Boltzmann constant and $T$ = 298 K).[12] This means that the variation of $\Delta E$ is well reflected in the difference in the activation free energy for the organotin-promoted electron transfer from (TPP)Co to $O_2$. The stronger the binding of organotins with $O_2^{\bullet-}$, the larger will be the promoting effects of organotins. Thus, $\Delta E$ can be regarded as good measure of the binding energies in the $O_2^{\bullet-}$ complexes with organotins as well as metal ions. No other methods have been able to determine the Lewis acidity in such a wide range as shown in Figure 2.[6]

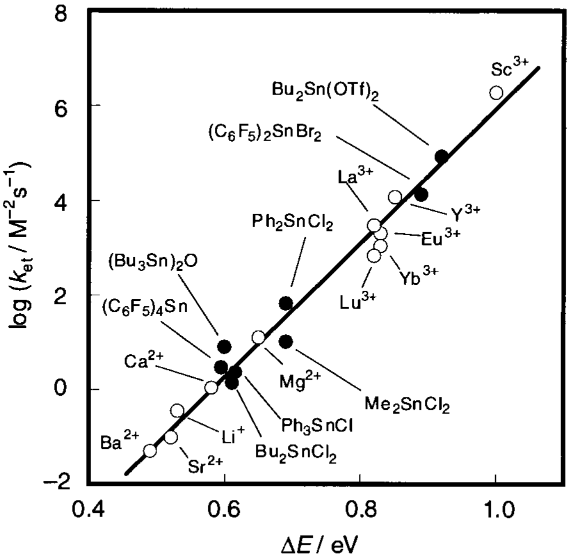


**Figure 2.** Plots of log $k_{et}$ vs $\Delta E$ in electron transfer from (TPP)Co to $O_2$, promoted by metal ions (triflate or perchlorate salts) (○) and organotin compounds (●) in MeCN at 298 K.

Judging from the $\Delta E$ values in Figure 2, the Lewis acidity of $(C_6F_5)_2SnBr_2$ is comparable to that of trivalent rare-earth metal ions except for $Sc(OTf)_3$. The Lewis acidity of $Bu_2Sn(OTf)_2$ or $(C_6F_5)_2SnBr_2$ is significantly larger than that of $Ph_2SnCl_2$, $Me_2SnCl_2$, $(Bu_3Sn)_2O$, $Ph_3SnCl$, $Bu_2SnCl_2$, or $(C_6F_5)_4Sn$ (Figure 2). This is consistent with the reported catalytic activity of these organotin compounds assessed for the aldol reaction of acetophenone with ketene silyl acetal in which $(C_6F_5)_2SnBr_2$ acts as an efficient catalyst whereas $(C_6F_5)_4Sn$ exhibited no activity.[2] It was confirmed in this study that $Bu_2Sn(OTf)_2$ also acted as a catalyst for carbon–carbon bond formation like the Mukaiyama-aldol reaction whereas other Lewis acids, $Ph_2SnCl_2$, $Me_2SnCl_2$, $(Bu_3Sn)_2O$, $Ph_3SnCl$, $Bu_2SnCl_2$, exhibited no catalytic activity under the same reaction conditions.

In summary, the $\Delta E$ values derived from the $g_{zz}$-values of the ESR spectra of the $O_2^{\bullet-}$ complexes with organotins as well as metal ions can be utilized as the first quantitative experimental measure to determine the Lewis acidity in relation with the catalytic effects in electron transfer reactions as well as in organic synthesis.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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12 The value is obtained from $1/(2.3kT) = (1.602 \times 10^{-19}\ \mathrm{J})/[2.3(1.381 \times 10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})] = 16.9$.