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Quantitative Evaluation of Lewis Acidity of Metal Ions with Different Ligands and Counterions in Relation to the Promoting Effects of Lewis Acids on Electron Transfer Reduction of Oxygen

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The g_{zz} values of ESR spectra of superoxide ($O_2^{\bullet -}$) complexes of metal ion salts acting as Lewis acids with different ligands and counterions were determined in acetonitrile at 143 K. The binding energies (ΔE) of $O_2^{\bullet -}$/Lewis acid complexes have been evaluated from deviation of the g_{zz} values from the free spin value. The ΔE value is quite sensitive to the difference in the counterions and ligands of metal ion salts acting as Lewis acids. On the other hand, the fluorescence maxima of the singlet excited states of 10-methylacridone/Lewis acid complexes are red-shifted as compared with that of 10-methylacridone, and the relative emission energies ($\Delta h\nu_f$) vary significantly depending on the Lewis acidity of metal ion salts with different counterions and ligands. The promoting effects of Lewis acids were also examined on electron transfer from cobalt(II) tetraphenylporphyrin to oxygen in acetonitrile at 298 K, which does not occur in the absence of Lewis acids under otherwise the same experimental conditions. Both ΔE and $\Delta h\nu_f$ values are well correlated with the promoting effects of Lewis acids on the electron transfer reduction of oxygen. Such correlations indicate that ΔE and $\Delta h\nu_f$ values can be used as quantitative measures of Lewis acidity of metal ion salts with different ligands and counterions. The Lewis acidity thus determined can also be applied to predict the promoting effects of Lewis acids on organic synthesis.

Introduction

Direct concerted reactions between singlet molecules and triplet oxygen ($^3O_2$: $^3\Sigma_g^-$) are spin-forbidden, whereas electron transfer from singlet electron donors to O_2 is spin-allowed. However, the electron transfer reduction of O_2 is rather difficult because of the low reduction potential of O_2.[1] In biological electron transfer systems such as that of respiration, the electron transfer reduction of O_2 is made possible by the catalytic function of metal enzymes.[2] There has been particular interest in the electron transfer mechanism of O_2 promoted by metal complexes.[3,4] We have previously reported that electron transfer reduction of O_2 has been made possible by strong binding of $O_2^{\bullet -}$ with metal triflates acting as Lewis acids.[5] The binding of $O_2^{\bullet -}$ with metal ions is confirmed by the ESR spectra of superoxide/metal ion complexes, the g_{zz} values of which are highly sensitive to the Lewis acidity of metal triflates.[5] The binding energies (ΔE) of metal triflates with $O_2^{\bullet -}$ can be determined from deviation of the g_{zz} value from free spin value.[5] The ΔE values are well correlated with the promoting effects of metal triflates on the electron transfer reduction of O_2.[5] The ΔE values can thereby be used as a quantitative measure for Lewis acidity of metal triflates in relation to the promoting effects in the electron transfer reduction of O_2.

The Lewis acidity of metal ions is expected to vary depending on the counterions and ligands. Metal ion salts with different counterions such as halides and organic ligands have frequently been utilized in promoting various reactions of synthetic value because of the high reactivities and selectivities achieved under the mild reaction conditions.[6−8] In particular, rare-earth metal triflates have attracted special attention, since only

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(1) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

(2) Kaim, W.; Schwederski, B. *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*; John Wiley & Sons: New York, 1991.

(3) Fukuzumi, S. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 4, pp 3−67.

(4) (a) Fukuzumi, S.; Ohtsu, H.; Ohkubo, K.; Itoh, S.; Imahori, H. *Coord. Chem. Rev.* **2002**, *226*, 71. (b) Fukuzumi, S. *Org. Biomol. Chem.* **2003**, *1*, 609.

(5) Fukuzumi, S.; Ohkubo, K. *Chem. Eur. J.* **2000**, *6*, 4532.

(6) (a) *Selectivities in Lewis Acid Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989. (b) Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC Press: Boca Raton, FL, 1995. (c) Yamamoto, H. *Lewis Acid Chemistry: A Practical Approach*; Oxford University Press: Oxford, 1999. (d) Denmark, S. E.; Almstead, N. G. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, Germany, 2000; Chapter 10.

(7) (a) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817. (b) Mukaiyama, T.; Murakami, M. *Synthesis* **1987**, 1043. (c) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (d) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.

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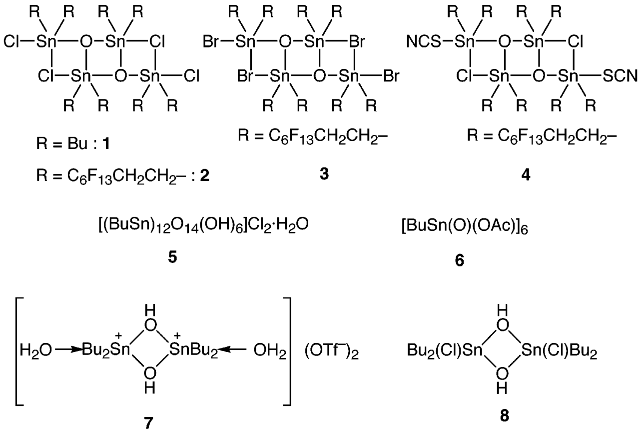
catalytic amounts of the triflates are required to catalyze a variety of synthetically useful reactions even in aqueous media as well as in many organic solvents.[8] However, Lewis acidity of metal ions with different counterions and ligands has yet to be evaluated quantitatively. On the other hand, neutral organotin halides, which have covalent bonding between tin and halogen atoms, and a variety of organotin dinuclear clusters have been utilized as mild tranesterification catalysts.[9,10] The Lewis acidity of dinuclear clusters as compared to mononuclear organotin compounds has yet to be evaluated quantitatively, either.

We report herein the ΔE values of $O_2^{\bullet -}$/metal ion salt complexes with different counterions and ligands, including mononuclear organotin compounds and dinuclear clusters, derived from the ESR spectra of $O_2^{\bullet -}$/metal ion salt complexes as a quantitative measure of Lewis acidity of metal ion salts, which varies depending on counterions and ligands. The fluorescence maxima of 10-methylacridone (AcrCO)/metal ion salt complexes can also be used as a quantitative measure of Lewis acidity, since the fluorescence energy ($h\nu_f$) decreases with increasing the Lewis acidity of metal ion salts.[11] Both the ΔE and $h\nu_f$ values are well correlated with promoting effects of metal ions with the corresponding counterions and ligands on the electron transfer reduction of O_2 in acetonitrile (MeCN). Since scandium triflate has been shown to be the strongest Lewis acid among metal triflates,[5,8,12,13] the effects of ligands on the Lewis acidity of metal ions are examined using scandium ions containing different ligands such as tetra-*p*-tolylporphyrin dianion (TTP^{2-}) and hexamethylphosphoric triamide (HMPA). The porphyrin is chosen as a ligand, since porphyrins are known to play very important roles in various biological processes such as photosynthesis and respiration.[14,15] Organotin compounds constitute another useful class of Lewis acids for the present purpose. They are sufficiently stable to give rise to structural diversity and to be manipulated for various measurements. The effects of counterions are examined using organotin halides, triflates, and organotin dinuclear clusters (Chart 1), which have been used as unique and useful Lewis acids to catalyze a variety of nucleophilic reactions of silyl and stannyl substrates under mild conditions.[16,17] Thus, the present study provides valuable information for quantitative measurement of the Lewis acidity of a variety of Lewis acids, which can be applied to predict the catalytic reactivity of Lewis acids in the Lewis acid-promoted organic synthesis.

CHART 1



$[(BuSn)_{12}O_{14}(OH)_6]Cl_2\cdot H_2O$ **5**

$[BuSn(O)(OAc)]_6$ **6**

Experimental Section

Materials. Butyldistannoxane and phenyltin derivatives were purchased commercially. Other organotin compounds were prepared according to the literature.[18−20] Scandium tetratolylporphyrin chloride ((TTP)ScCl, TTP^{2-} = dianion of tetra-*p*-tolylporphyrin) was prepared as described in the literature.[21] Cobalt(II) tetraphenylporphyrin, (TPP)Co, was prepared as described in the literature.[22] The dimeric 1-benzyl-1,4-dihydronicotinamide $[(BNA)_2]$ was prepared according to the literature.[23−25] Scandium triflate $[Sc(OTf)_3]$ and 10-methylacridone were obtained commercially. Hexamethylphosphoric triamide (HMPA) was purchased commercially and purified by the standard method.[26] Acetonitrile (MeCN), benzonitrile (PhCN), and tetrahydrofuran (THF) used as solvents were purified and dried by the standard procedure.[26]

Spectral Measurements. The fluorescence measurements of AcrCO/Lewis acid complexes were performed on a spectrofluorophotometer. The excitation wavelength of AcrCO/Lewis acid complexes was 413 nm in MeCN. The MeCN solutions

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(8) (a) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227. (b) Kobayashi, S.; Manabe, K. *Acc. Chem. Res.* **2002**, *35*, 209. (b) Kobayashi, S. *Eur. J. Org. Chem.* **1962**, *27*, 7.

(9) (a) Otera, J. In *Advances in Detailed Reaction Mechanism*; Coxon, J. M., Ed.; JAI Press: Greenwich; 1994; p 167. (b) Orita, A.; Mitsutome, A.; Otera, J. *J. Org. Chem.* **1998**, *63*, 2420. (c) Xiang, J.; Toyoshima, S.; Orita, A.; Otera, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3670. (d) Xiang, J.; Orita, A.; Otera, J. *Angew. Chem., Int. Ed.* **2002**, *42*, 4117.

(10) (a) Orita, A.; Hamada, Y.; Nakano, T.; Toyoshima, S.; Otera, J. *Chem. Eur. J.* **2001**, *7*, 3321. (b) Durnd, S.; Sakamoto, K.; Fukuyama, T.; Orita, A.; Otera, J.; Duthie, A.; Dakternieks, D.; Shulte, M.; Jurkschat, K. *Organometallics* **2000**, *19*, 3220.

(11) A preliminary report has appeared; see: Fukuzumi, S.; Ohkubo, K. *J. Am. Chem. Soc.* **2002**, *124*, 10270.

(12) (a) Fukuzumi, S.; Fujii, Y.; Suenobu, T. *J. Am. Chem. Soc.* **2001**, *123*, 10191. (b) Fukuzumi, S.; Mori, H.; Imahori, H.; Suenobu, T.; Araki, Y.; Ito, O.; Kadish, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 12458.

(13) (a) Fukuzumi, S.; Ohkubo, K.; Okamoto, T. *J. Am. Chem. Soc.* **2002**, *124*, 14147. (b) Fukuzumi, S.; Inada, O.; Satoh, N.; Suenobu, T.; Imahori, H. *J. Am. Chem. Soc.* **2002**, *124*, 9181. (c) Fukuzumi, S.; Yuasa, J.; Suenobu, T. *J. Am. Chem. Soc.* **2002**, *124*, 12566.

(14) Fukuzumi, S. Electron Transfer Chemistry of Porphyrin and Metalloporphyrins. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R.; Eds.; Academic Press: San Diego, 2000; Vol. 8, Chapter 56.

(15) Fukuzumi, S.; Imahori, H. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 2, pp 927−975.

(16) (a) Sato, T.; Otera, J.; Nozaki, H. *J. Am. Chem. Soc.* **1990**, *112*, 901. (b) Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H.; Fukuzumi, S. *J. Am. Chem. Soc.* **1991**, *113*, 4028. (c) Sato, T.; Wakahara, Y.; Otera, J.; Nozaki, H. *Tetrahedron* **1991**, *47*, 9773. (d) Chen, J.; Otera, J. *Angew. Chem., Int. Ed.* **1998**, *37*, 91. (e) Chen, J.; Sakamoto, K.; Orita, A.; Otera, J. *J. Org. Chem.* **1998**, *63*, 9739.

(17) (a) Chen, J.; Sakamoto, K.; Orita, A.; Otera, J. *J. Organomet. Chem.* **1999**, *574*, 58. (b) Chen, J.; Sakamoto, K.; Orita, A.; Otera, J *Tetrahedron* **1998**, *54*, 8411.

(18) Chen, J.-x.; Sakamoto, K.; Orita, A.; Otera, J. *J. Organomet. Chem.* **1999**, *574*, 58.

(19) Orita, A.; Xiang, J.; Sakamoto, K.; Otera, J. *J. Organomet. Chem.* **2001**, *624*, 287.

(20) (a) Sakamoto, K.; Ikeda, H.; Akashi, H.; Fukuyama, T.; Orita, A.; Otera, J. *Organometallics* **2000**, *19*, 3242. (b) Xiang, J.; Orira, A.; Otera, J. *J. Organomet. Chem.* **2002**, *648*, 246. (c) Xiang, J.; Toyoshima, S.; Orita, A.; Otera, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3670.

(21) Dewchok, M. G.; Haushalter, R. C.; Merola, J. S. *Inorg. Chim. Acta* **1988**, *144*, 47.

(22) Adler, A. D.; Longo, F. R.; Váradi, V. *Inorg. Synth.* **1976**, *16*, 213.

(23) Wallenfels, K.; Gellerich, M. *Chem. Ber.* **1959**, *92*, 1406.

(24) Patz, M.; Kuwahara, Y.; Suenobu, T.; Fukuzumi, S. *Chem. Lett.* **1997**, 567.

(25) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito. O. *J. Am. Chem. Soc.* **1998**, *120*, 8060.

(26) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 4th ed.; Pergamon Press: Elmsford, NY, 1996.

TABLE 1. g_{zz} and ΔE Values of ESR Spectra of $O_2^{\bullet-}$/Lewis Acid Complexes, $\Delta h\nu_f$ Values of ^{1}AcrCO*/Lewis Acid Complexes, and Rate Constants (k_{et}) for Lewis Acid-Promoted Electron Transfer from (TPP)Co to O_2

entry	Lewis acid	ΔE (eV)	g_{zz}	λ_{max} (nm)	$\Delta h\nu_f$ (eV)	k_{et} ($M^{-2}\ s^{-1}$)
1	$Bu_2Sn(OTf)_2$	0.92	2.0327	471	0.24	8.8×10^4
2	$(C_6F_5)_2SnBr_2$	0.89	2.0336	470	0.23	1.4×10^4
3	$(C_6F_5)_2SnCl_2$	0.88	2.0341	470	0.23	1.3×10^4
4	Ph_2SnCl_2	0.69	2.0428	447	0.10	6.9×10
5	Me_2SnCl_2	0.69	2.0429			1.1×10
6	$(C_6F_5)_3SnCl$	0.67	2.0439	449	0.11	1.2×10
7	$(C_6F_5)_3SnBr$	0.65	2.0454	452	0.13	9.0
8	**1**	0.63	2.0467			6.3
9	Ph_3SnCl	0.62	2.0477	455	0.15	2.4
10	Bu_2SnCl_2	0.61	2.0479	453	0.13	1.4
11	$(Bu_3Sn)_2O$	0.60	2.0493			8.1
12	$(C_6F_5)_4Sn$	0.59	2.0494			3.0
13	**5**	0.43	2.0555			a
14	BuSn(:O)OH	0.51	2.0576			a
15	**7**	0.49	2.0595			a
16	**8**	0.43	2.0667	434	0.01	a
17	**3**	0.42	2.0696	433	0.01	a
18	**2**	0.38	2.0757	432	0.00	a
19	**4**	0.37	2.0777	433	0.01	a
20	**6**	0.32	2.0891	432	0.00	a
21	$Sc(OTf)_3$	1.00	2.0304	474	0.25	1.9×10^6
22	(TTP)ScCl	0.76	2.0390			1.8×10^3
23	$(HMPA)_3Sc(OTf)_3$	0.72	2.0413			3.7×10^2

[a] Too slow to be determined accurately.

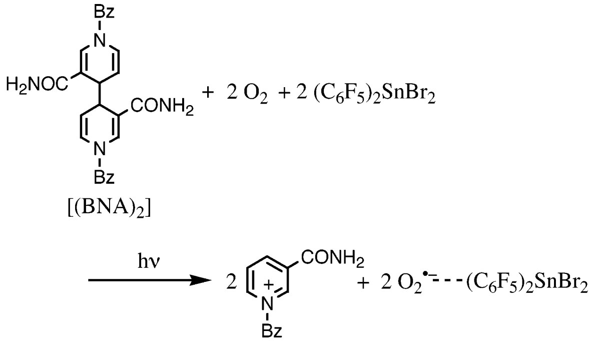
were deaerated by argon purging for 7 min prior to the measurements.

Kinetic measurements for electron transfer from (TPP)Co to oxygen were carried out using a photodiode array spectrophotometer at 298 K. The rates of the electron transfer were followed by spectrally monitoring the disappearance and rise of the absorption bands at 412 and 433 nm due to the decay of (TPP)Co and the formation of (TPP)Co^+, respectively. The rate constants of electron transfer were determined by pseudo-first-order plots for the electron transfer reactions in the presence of a large excess of oxygen and Lewis acid. It was confirmed that the pseudo-first-order rate constant was proportional to the oxygen and Lewis acid concentrations. The k_{et} values in Table 1 were determined within an experimental error of ±5%.

ESR Measurements. A quartz ESR tube (4.5 mm i.d.) containing an oxygen-saturated MeCN solution of $(BNA)_2$ (1.0×10^{-3} M) and a Lewis acid (1.0×10^{-3} M) was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. The ESR spectra of $O_2^{\bullet-}$/Lewis acid complexes in frozen MeCN were measured at 143 K with an X-band spectrometer using an attached VT (variable-temperature) apparatus under nonsaturating microwave power conditions. The g values were calibrated precisely with an Mn^{2+} marker that was used as a reference.

Results and Discussion

ESR Spectra of $O_2^{\bullet-}$/Lewis Acid Complexes in Frozen Solution. Superoxide ion ($O_2^{\bullet-}$) is produced by the photoinduced reduction of O_2 by dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$], which acts as a two-electron donor to reduce 2 equiv of O_2 to $O_2^{\bullet-}$.[27] In the presence of Lewis acid (e.g., $(C_6F_5)_2SnBr_2$), the $O_2^{\bullet-}$/Lewis acid complex is formed as shown in eq 1.[28]



(1)

The $O_2^{\bullet-}/(C_6F_5)_2SnBr_2$ complex formed photochemically is detected by the ESR spectroscopy at 143 K as shown in Figure 1a (see Experimental Section). The ESR spectrum showed a typical anisotropic signal with $g_{zz} = 2.0336$ and $g_{xx} = g_{yy} = 2.0060$. Similarly, ESR spectra of a variety of $O_2^{\bullet-}$/Lewis acid complexes were measured under the same experimental conditions. The g_{zz} values of $O_2^{\bullet-}$/Lewis acid complexes are quite different depending on the Lewis acidity. For example, the g_{zz} value of the $O_2^{\bullet-}/(C_6F_5)_4Sn$ complex is 2.0494 (Figure 1b), which is significantly larger than the value of the $O_2^{\bullet-}/(C_6F_5)_2SnBr_2$ complex (Figure 1a). When a tin cluster (**6**) is employed as a Lewis acid, the g_{zz} value of the $O_2^{\bullet-}$/**6** complex is further increased to 2.0891 (Figure 1c).

Scandium ion is the most effective as compared to other metal ions in various electron transfer reactions[5,12–14] and can bind with $O_2^{\bullet-}$ most strongly. The ESR spectrum of the $O_2^{\bullet-}/Sc(OTf)_3$ complex in MeCN at 143 K is shown in Figure 2a. The anisotropic g values are determined as $g_{zz} = 2.0304$, $g_{xx} = 2.0095$, and $g_{yy} = 2.0040$. The eight-line superhyperfine coupling of $O_2^{\bullet-}$ with the 7/2 nuclear spin of the scandium nucleus is clearly seen around each g component in the anisotropic signal, demonstrating the spin delocalization to the scandium nucleus due to the binding of $Sc(OTf)_3$ with $O_2^{\bullet-}$. Computer simulation spectrum of the $Sc(OTf)_3/O_2^{\bullet-}$ complex is also shown in

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[27] Fukuzumi, S.; Patz, M.; Suenobu, T.; Kuwahara, Y.; Itoh, S. *J. Am. Chem. Soc.* **1999**, *121*, 1605.

[28] Lewis acid is defined as a substance that binds with a base such as $O_2^{\bullet-}$, and the Lewis acidity is determined by the binding strength.

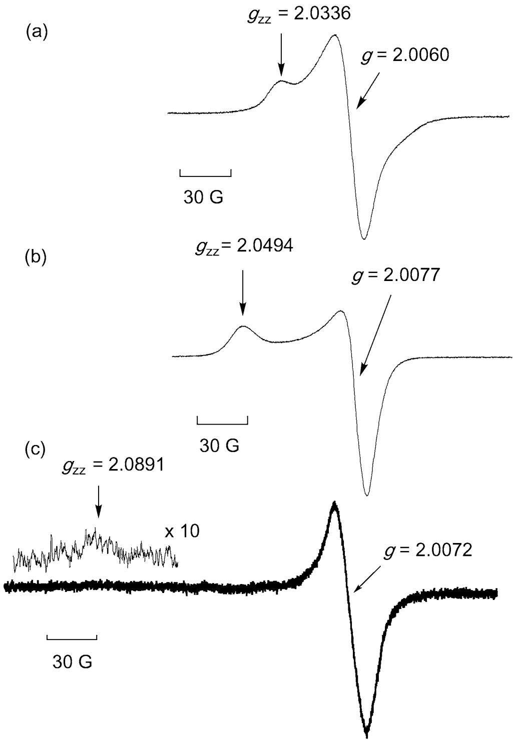

FIGURE 1. ESR spectra of (a) $O_2^{\bullet-}/(C_6F_5)_2SnBr_2$, (b) $O_2^{\bullet-}/(C_6F_5)_4Sn$, and (c) $O_2^{\bullet-}$/**6** in frozen MeCN at 143 K.

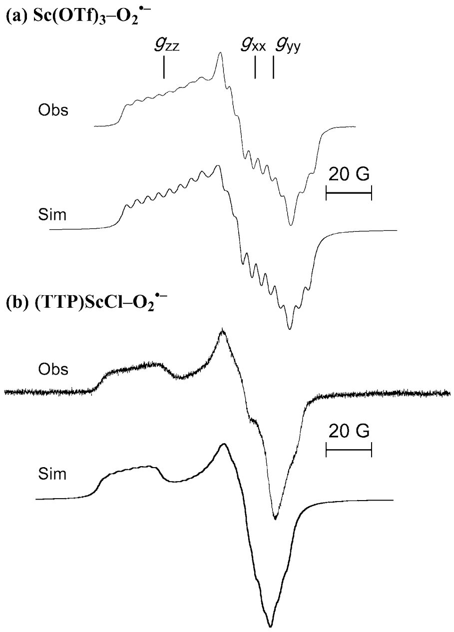

FIGURE 2. ESR spectra of (a) the $O_2^{\bullet-}/Sc(OTf)_3$ complex in frozen MeCN and (b) the $O_2^{\bullet-}$/(TTP)ScCl complex in frozen THF at 143 K and their computer simulation spectra.

Figure 2a. The superhyperfine coupling constants are determined as $A_{zz}(Sc) = 4.1$ G, $A_{xx}(Sc) = 3.4$ G, and $A_{yy}(Sc) = 3.6$ G.

Similarly, an ESR spectrum of the (TTP)ScCl/$O_2^{\bullet-}$ complex (TTP^{2-} = dianion of tetra-*p*-tolylporphyrin) is observed under photoirradiation of (TTP)ScCl with $(BNA)_2$ in the presence of O_2 at 143 K as shown Figure 2b. Although the superhyperfine structure due to the scandium nucleus is not well resolved, the computer simulation spectrum afforded the superhyperfine coupling constants as $A_{zz}(Sc) = 3.6$ G, $A_{xx}(Sc) = 3.3$ G, and $A_{yy}(Sc) = 3.9$ G. The anisotropic g values are determined as $g_{zz} = 2.0390$, $g_{xx} = 2.0095$, and $g_{yy} = 2.0004$, which are coaxial with the superhyperfine tensor. Although the ESR signal of $O_2^{\bullet-}$ cannot be detected in solution at room temperature due to the line-broadening resulting from the fast relaxation,[29] the ESR signal of the (TTP)ScCl/$O_2^{\bullet-}$ complex is detected in THF at room temperature (see Supporting Information, S1). The isotropic g value (2.0175) agrees with the average value of three anisotropic g components. The superhyperfine coupling constant (3.63 G) also agrees with the average value of three anisotropic values.

The ESR parameters of the $O_2^{\bullet-}/(HMPA)_3Sc(OTf)_3$ complex are also determined as $g_{zz} = 2.0413$, $g_{xx} = 2.0095$, $g_{yy} = 2.0004$, $g = 2.0165$, $A_{zz}(Sc) = 3.6$ G, $A_{xx}(Sc) = 3.3$ G, and $A_{yy}(Sc) = 3.9$ G.

Comparison of the g_{zz} values in Figures 1 and 2 reveals that the g_{zz} values are highly sensitive to differences in metal ions, counterions, and ligands, including clusters. The g_{zz} values were determined for a variety of $O_2^{\bullet-}$/Lewis acid complexes, and the results are listed in Table 1.

The g tensor, in particular the g_{zz} value, gives valuable information concerning the binding strength between $O_2^{\bullet-}$ and Lewis acids. 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,[30]

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

where λ is the spin–orbit coupling constant of oxygen, which is known to be 0.014 eV,[31] and ΔE is the energy splitting of π_g levels due to the complex formation between $O_2^{\bullet-}$ and Lewis acids. Under the conditions that $\Delta E \gg \lambda$, eq 2 is reduced to a simple relation, $g_{zz} = g_e + 2\lambda/\Delta E$. Thus, the ΔE values of $O_2^{\bullet-}$ complexes with a variety of Lewis acids are determined from the deviation of the g_{zz} values from the g_e value as listed in Table 1. The largest ΔE value is obtained for $Sc(OTf)_3$ and the smallest ΔE value is obtained for a tin cluster (**6**).

Fluorescence Spectra of AcrCO/Lewis Acid Complexes. 10-Methylacridone is known to form complexes with a variety of Lewis acids.[32] Irradiation of the absorption band of 10-methylacridone (AcrCO) results in fluorescence at 432 nm in MeCN.[33] The fluorescence maxima of the singlet excited states of the complexes ($^1AcrCO^*$/Lewis acid) are red-shifted and vary significantly depending on the Lewis acidity (Scheme 1) as shown in Figure 3.

This indicates that the binding of Lewis acids with the singlet excited state of AcrCO is much stronger than the binding with the ground state and that the difference in

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[29] Bagchi, R. N.; Bond, A. M.; Scholz, F.; Stösser, R. *J. Am. Chem. Soc.* **1989**, *111*, 8270.

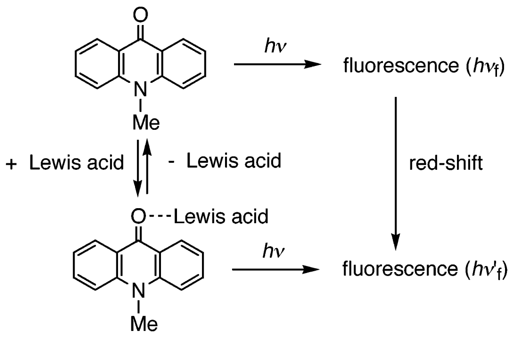
[30] (a) Känzig W.; Cohen, M. H. *Phys. Rev. Lett.* **1959**, *3*, 509. (b) Zeller, H. R.; Kanzig, W. *Helv. Phys. Acta* **1967**, *40*, 845.

[31] Kasai, P. H. *J. Chem. Phys.* **1965**, *43*, 3322.

[32] Fukuzumi, S.; Satoh, N.; Okamoto, T.; Yasui, K.; Suenobu, T.; Seko, Y.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2001**, *123*, 7756.

[33] Fukuzumi, S.; Fujita, M.; Otera, J. *J. Org. Chem.* **1993**, *58*, 5405.

SCHEME 1



the binding energy between the ground and excited state increases with increasing Lewis acidity.[34] The two emission bands in Figure 3 correspond to the energy splitting due to the coupling of CO stretching in the ^{1}AcrCO*/Lewis acid complex. The emission maxima (λ_{max}) of the ^{1}AcrCO* complexes with a series of Lewis acids employed for determination of ΔE (vide supra) and the emission energy difference ($\Delta h\nu_f$) between ^{1}AcrCO* ($h\nu_f = 2.87$ eV) and the ^{1}AcrCO*/Lewis acid complexes are also listed in Table 1. The largest $\Delta h\nu_f$ and ΔE values are obtained for Sc(OTf)$_3$, and the smallest $\Delta h\nu_f$ and ΔE values are obtained for a tin cluster (**6**). The $\Delta h\nu_f$ values of ^{1}AcrCO*/Lewis acid complexes are linearly correlated with the ΔE values of the corresponding Lewis acid/$O_2^{\bullet-}$ complexes as shown in Figure 4 (eq 3).

$$\Delta h\nu_f\,(\mathrm{eV}) = 0.383\,\Delta E\,(\mathrm{eV}) + -0.13 \qquad (3)$$

The stronger the acidity of the Lewis acid, the larger are the $h\nu_f$ and ΔE values. Thus, both the $h\nu_f$ and ΔE values can be used as a quantitative measure of the acidity of a variety of Lewis acids.

Lewis Acid-Promoted Electron Transfer. No electron transfer from (TPP)Co ($E^0_{ox} = 0.35$ V vs SCE in MeCN)[35] to O_2 ($E^0_{red} = -0.86$ V vs SCE in MeCN)[36] has occurred in MeCN at 298 K. When the binding of $O_2^{\bullet-}$ with a Lewis acid is sufficiently strong, electron transfer from (TPP)Co to O_2 becomes energetically feasible as shown in Scheme 2. In fact, metal ions have been reported to promote electron transfer from (TPP)Co (TPP^{2-} = dianion of tetraphenylporphyrin) to O_2 in MeCN.[3-5] Thus, to assess a relation between the ΔE value and promoting effects of Lewis acid in the electron transfer reduction of O_2, the rates of electron transfer from (TPP)Co to O_2 were determined in the presence of a series of Lewis acids by the UV−vis spectral change for the decay of (TPP)Co ($\lambda_{max} = 411$ nm) as well as the formation of $[(TPP)Co]^+$ ($\lambda_{max} = 434$ nm) in MeCN at 298 K. A typical example for such spectral change is shown in Figure 5 for an efficient electron transfer from (TPP)Co to O_2 in the presence of $(C_6F_5)_2SnBr_2$.

The electron transfer rates obeyed second-order kinetics, showing a first-order dependence on each concentration of (TPP)Co and O_2 (see Supporting Information S2).

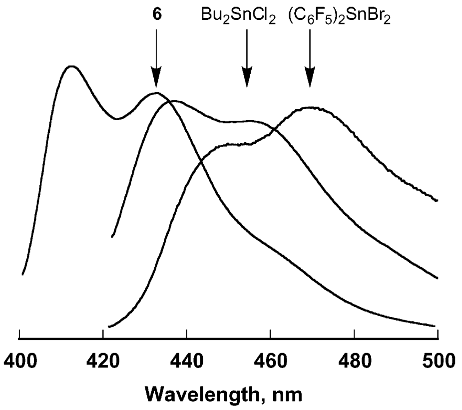


FIGURE 3. Fluorescence spectra of the ^{1}AcrCO*/Lewis acid complexes in deaerated MeCN at 298 K.

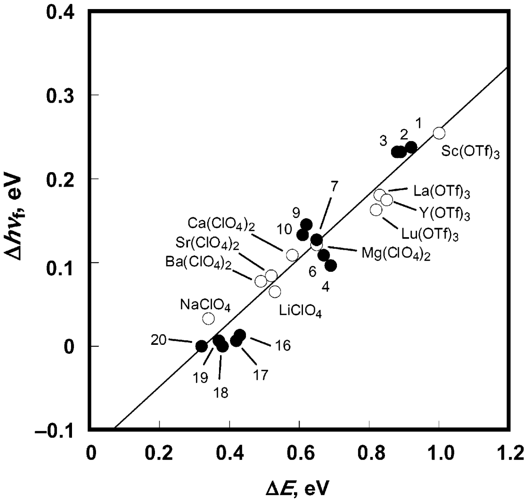
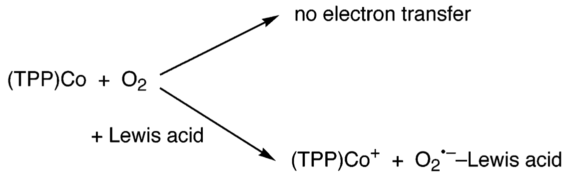


FIGURE 4. Plot of $\Delta h\nu_f$ of the ^{1}AcrCO*/Lewis acid complexes vs ΔE derived from the g_{zz} values of the ESR spectra of the $O_2^{\bullet-}$/Lewis acid complexes in MeCN. Numbers refer to the Lewis acid entries in Table 1. The data of other metal ion salts in ref 11 are also combined in the figure.

SCHEME 2



The observed second-order rate constant (k_{obs}) for the Lewis acid-promoted electron transfer increases linearly with increasing Lewis acid concentration (S3). The rate constant of Lewis acid-promoted electron transfer (k_{et}) is determined from the slope of the linear plot of k_{obs} vs [Lewis acid] and the k_{et} values are also listed in Table 1.

Relation between Lewis Acidity and Catalytic Reactivity. $Bu_2Sn(OTf)_2$ (entry 1) exhibits the largest k_{et}, ΔE, and $\Delta h\nu_f$ values among the tin compounds in Table 1. When the counterion (OTf^-) is replaced by Cl^- (entry 10), the k_{et}, ΔE, and $\Delta h\nu_f$ values become significantly smaller due to the strong covalent bond between tin and halogen atoms, which decreases the Lewis acidity of Bu_2SnCl_2. There is only a slight difference in the Lewis

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[34] Absorption spectra of AcrCO are also red-shifted due to the complexation with Lewis acids.[32]

[35] Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *Inorg. Chem.* **1989**, *28*, 2459.

[36] Sawyer, D. T.; Calderwood, T. S.; Yamaguchi, K.; Angelis, C. T. *Inorg. Chem.* **1983**, *22*, 2577.

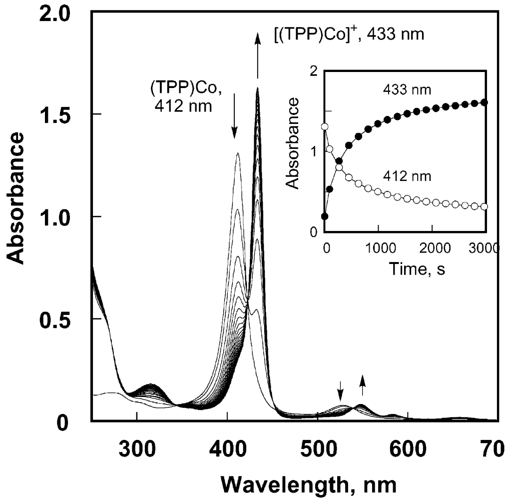

FIGURE 5. Electronic absorption spectral change observed in electron transfer from (TPP)Co (9.0×10^{-6} M) to O_2 (air saturated, 2.6×10^{-3} M) in the presence of $(C_6F_5)_2SnBr_2$ (5.4×10^{-5} M) in MeCN at 298 K; time intervals = 180 s.

acidity between $(C_6F_5)_2SnBr_2$ (entry 2) and $(C_6F_5)_2SnCl_2$ (entry 3) judging from the similar k_{et}, ΔE, and $\Delta h\nu_f$ values. Thus, the difference in the counterion between Cl^- and Br^- results in little change in the Lewis acidity of organotin halides. On the other hand, a decrease in the number of halide ions (Cl^- or Br^-) results in a decrease in the Lewis acidity of organotin halides judging from the decreasing order of k_{et}, ΔE, and $\Delta h\nu_f$ values: $(C_6F_5)_2SnX_2$ (entries 2 and 3) > $(C_6F_5)_3SnX$ (entries 6 and 7) > $(C_6F_5)_4Sn$ (entry 12).

When C_6F_5 group is replaced by Ph, the Lewis acidity of Ph_nSnCl_{4-n} ($n = 2, 3$; entries 4 and 9) becomes weaker as compared with that of $(C_6F_5)_nSnCl_{4-n}$ (entries 3 and 6) due to electron-withdrawing effects of fluorine atoms. Organotin dimers, clusters (entires 13 and 15−20), and BuSn(:O)OH (entry 14) exhibit weak Lewis acidity as compared to Bu_2SnCl_2 (entry 10) except for **1** (entry 8) (vide infra). In the case of entries 13−20 in Table 1, the rates of electron transfer from (TPP)Co to O_2 were too slow to be determined accurately.

In the case of Sc^{3+} ion, the Lewis acidity decreases in the order $Sc(OTf)_3$ > (TTP)ScCl > $(HMPA)_3Sc(OTf)_3$. The addition of HMPA ligand to $Sc(OTf)_3$ results in a significant decrease in the Lewis acidity due the electron-donating effect of HMPA. The addition of TTP^{2-} ligand also results in a decrease in the Lewis acidity of Sc^{3+} ion.

There is a striking single linear correlation between log k_{et} and ΔE of the $O_2^{\bullet -}$/Lewis acid complexes as shown in Figure 6, where the k_{et} and ΔE values of various metal ion triflates reported previously[5] are included. 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 ΔE is obtained as 14.0, which is close to the value of $1/(2.3k_BT)$ (= 16.9, where k_B is the Boltzmann constant and T = 298 K).[37] This means that the variation of ΔE is well reflected in the difference in the activation free energy for the Lewis acid-promoted electron transfer from (TPP)Co to O_2. The stronger the binding of Lewis acids with $O_2^{\bullet -}$, the larger the promoting effects of Lewis acids. Thus, ΔE can be regarded as the binding energy in $O_2^{\bullet -}$/Lewis acid complexes. Since there is a good linear correlation between ΔE of $O_2^{\bullet -}$/Lewis acid complexes and $\Delta h\nu_f$ of ^{1}AcrCO*/Lewis acid complexes, both the ΔE and $\Delta h\nu_f$ values can be used as quantitative measures of the Lewis acidity of metal ion salts with different counterions and ligands.

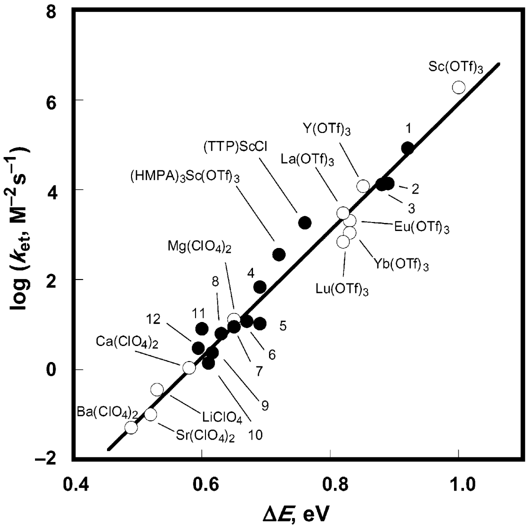

FIGURE 6. Plots of log k_{et} vs ΔE in electron transfer from (TPP)Co to O_2, promoted by metal ions (triflate or perchlorate salts) (○) and organotin compounds and scandium complexes (●) in MeCN at 298 K. Numbers refer to Lewis acid entries in Table 1. The data of other metal ion salts in ref 5 are also combined in the figure.

Judging from the ΔE values in Figure 6, 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 $Bu_2Sn(OTf)_2$, $(C_6F_5)_2SnBr_2$, or $(C_6F_5)_2SnCl_2$ 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 6). 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 $(C_6F_5)_2SnBr_2$ and $Sc(OTf)_3$ acts as an efficient catalyst, whereas $(C_6F_5)_4Sn$ exhibited no activity.[18] $Bu_2Sn(OTf)_2$ also acts as a catalyst for carbon−carbon bond formation with various silyl nucleophiles,[16a−c] 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.[38] Thus, it may be safe to conclude that Lewis acids with the ΔE values larger than 0.88 are capable for inducing carbon−carbon bond-forming reactions.[39] On the other hand, relatively weak Lewis acids such as oganotin dimers and clusters (entries 13 and 15−20) have been utilized as transesterfication as well as esterification catalysts under mild reaction conditions where a variety of functional groups are tolerated.[9,10] Among them, fluoroalkyldistannoxanes **2**−**4**, which are efficient fluorous

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(37) Value is obtained from $1/(2.3k_BT) = (1.602 \times 10^{-19}\ \text{J})/[2.3(1.381 \times 10^{-23}\ \text{J/K})(298\ \text{K})] = 16.9$.

(38) Ohkubo, K.; Suenobu, T.; Imahori, H.; Orita, A.; Otera, J.; Fukuzumi, S. *Chem. Lett.* **2001**, 978.

(39) An exception appeared for a relatively small ΔE value of $(C_6F_5)_3SnBr$, which catalyzed Mukaiyama-aldol reaction with a ketene silyl acetal.[18] We suppose that this anomaly may be attributable to the unique character of the perfluorophenyl group. See ref 18 for unusual reactivities of perfluorophenyltin compounds.

biphasic (trans)esterification catalysts[9c,d], deserve to be discussed in more detail. Partially fluorinated alkyl groups such as $C_nF_{2n+1}(CH_2)_m$ ($m = 1-3$) are employed in fluorous biphase technology because the fluoroalkyl moiety serves for endowment of fluorophilicity, while the methylene spacer insulates the influence of the strong electron-withdrawing effect of the fluoroalkyl part so that the innate character of the central element could be preserved.[40] The small ΔE values of **2**−**4** compared with **1** offer strong support for such insulation. It is further noteworthy that the ΔE value obtained for **1** is comparable to that of Bu_2SnCl_2, although the former exhibits much higher catalytic activities. This is consistent with a view that the template effect induced by proximately located tin atoms in **1** plays a key role despite its low acidity.[9a]

Summary and Conclusions

The ΔE values derived from the g_{zz} values of the ESR spectra of the $O_2^{\bullet -}$/Lewis acid complexes and the $\Delta h\nu_f$ values of ^{1}AcrCO*/Lewis acid complexes can be utilized as quantitative measures of the Lewis acidity of metal ion salts with different counterions and ligands in relation with the promoting effects of Lewis acids in electron transfer reactions as well as in organic synthesis. The Lewis acidity of metal ion salts can be finely controlled by the binding strength of counterions and electronic effects of ligands. We hope that the ΔE and $\Delta h\nu_f$ values presented herein will provide a new proving ground for the study of reactivities and mechanisms of Lewis acid-promoted reactions.

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Supporting Information Available: ESR spectrum of the (TTP)ScCl/$O_2^{\bullet -}$ complex in THF at room temperature (S1) and kinetic data for Lewis acid/promoted electron transfer from (TPP)Co to O_2 (S2 and S3). This material is available free of charge via the Internet at http://pubs.acs.org.

JO034258U

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[40] Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641.