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Fluorescence Maxima of 10-Methylacridone−Metal Ion Salt Complexes: A Convenient and Quantitative Measure of Lewis Acidity of Metal Ion Salts

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A variety of metal ion salts have been employed to promote reactions of nucleophiles with electrophiles which can be activated by the coordination of metal ion salts to electrophiles, controlling not only the reactivities but also the selectivities.[1−4] Metal ion salts can also promote free radical reactions and electron-transfer reactions.[5−8] The promoting effects of metal ions are certainly related to the Lewis acidity of metal ion salts employed to promote the reactions. The Lewis acidity of metal ions can be predicted qualitatively on the basis of the charges and ion radii of metal ions. However, it is highly desired to have a *quantitative* measure of the Lewis acidity of metal ions in relation with the promoting effects on the reactions.

We have recently reported that the g_{zz} values of ESR spectra of superoxide−metal ion complexes are highly sensitive to the Lewis acidity of a variety of metal ions and that the binding energies (ΔE) readily derived from the g_{zz} values provide a quantitative measure of Lewis acidity of metal ions.[9,10] The ΔE values have been shown to be directly correlated with the promoting effects of metal ions in electron-transfer reactions.[9,10] However, this method can only be applied to diamagnetic metal ions, since the paramagnetic metal ion complexes with $O_2^{\bullet -}$ give no ESR signal. Redox active metal ions which undergo electron-transfer reactions with $O_2^{\bullet -}$ cannot be employed, either.

We report herein a much more general and convenient method to provide a quantitative measure of the Lewis acidity of metal ion salts. That is the fluorescence maxima of 10-methylacridone (AcrCO)−metal ion salt complexes. The florescence energy ($h\nu_f$) decreases with increasing the Lewis acidity of metal ion salts, and the $h\nu_f$ value provides quantitative measure of the Lewis acidity of metal ions including paramagnetic and redox active species.

Irradiation of the absorption band of AcrCO results in fluorescence at 432 nm in MeCN. When $Sc(OTf)_3$ is added to an MeCN solution of AcrCO, the absorption band of AcrCO is red-shifted due to the 1:1 complex formation between AcrCO and $Sc(OTf)_3$.[11] The formation constant (K) is determined from the spectral change as 1.2×10^5 M^{-1}.[11] Thus, the Lewis acidity of $Sc(OTf)_3$ is strong enough to form the complex with AcrCO in competition with the coordination of MeCN which is an abundant weak base. When AcrCO forms the complex with $Sc(OTf)_3$, the fluorescence maximum (λ_{max}) is red-shifted from 432 to 474 nm, and the fluorescence lifetime (τ) becomes longer in the AcrCO−$Sc(OTf)_3$ complex (16.9 ns for the $^1AcrCO^*$−$Sc(OTf)_3$ complex and 6.1 ns for $^1AcrCO^*$).[11] Similarly the fluorescence spectra were observed when AcrCO forms the complexes with various metal ions (M^{n+}) including paramagnetic and redox active metal ion salts such as $Fe(ClO_4)_3$, $Cu(ClO_4)_2$, $Mn(ClO_4)_2$, and $Co(ClO_4)_2$ (typical examples are shown in Figure 1). The two absorption bands in Figure 1 correspond to the energy splitting due to the coupling of CO stretching in the $^1AcrCO^*$−M^{n+} complex. The absorption maxima (λ_{max}), $h\nu_f$ and τ values are listed in Table 1.

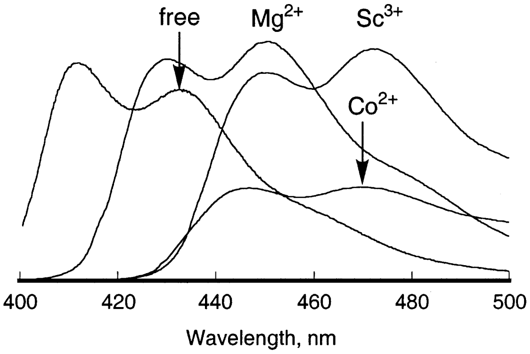

Figure 1. Fluorescence spectra of AcrCO and the AcrCO−M^{n+} complexes in deaerated MeCN at 298 K.

Organotin halides, in particular, pentafluorophenyltin bromides 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.[12] The pentafluorophenyltin bromides and other organotin halides also form the complexes with AcrCO and the λ_{max}, $h\nu_f$ and τ values of the $^1AcrCO^*$−Lewis acid complexes are also listed in Table 1.

The g_{zz}-value of the ESR spectrum of the $O_2^{\bullet -}$−Lewis acid complex gives valuable information concerning the binding strength of the $O_2^{\bullet -}$−Lewis acid complex. 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 1,

$$g_{zz} = g_e + 2\lambda/\Delta E \qquad (1)$$

where λ is the spin−orbit coupling constant (0.014 eV) and ΔE is the energy splitting of π_g levels due to the complex formation between $O_2^{\bullet -}$ and Lewis acid, and $\Delta E \gg \lambda$.[9,10] Thus, the ΔE values are readily determined from the deviation of the g_{zz}-values from the free spin value (g_e) as listed in Table 1.[9,10] The ΔE values derived from the g_{zz}-values of ESR spectra of the $O_2^{\bullet -}$−Lewis acid complexes can be used as a quantitative measure of Lewis acidity of the metal ion salt including organotin halides, since the rate constants (k_{et}) of Lewis acid-promoted electron transfer from an one-electron reductant such as (TPP)Co (TPP^{2-} = tetraphenylporphyrin dianion) to O_2 is well-correlated with the ΔE values.[9,10]

There is a *striking linear correlation* between the $h\nu_f$ values of $^1AcrCO^*$−Lewis acid complexes and the ΔE values of the $O_2^{\bullet -}$−Lewis acid complexes derived from the g_{zz}-values as shown in

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Table 1. Fluorescence Maxima (λ_{max}), the Energies ($h\nu_f$), the Lifetimes (τ) of the ^{1}AcrCO*−Lewis Acid Complexes and the Binding Energies (ΔE) of the $O_2^{\bullet -}$−Lewis Acid Complexes

Lewis acid	ΔE, eV[a]	λ_{max}, nm	$h\nu_f$, eV	τ, ns
$Sc(OTf)_3$	1.00	474	2.62	16.9
$Y(OTf)_3$	0.85	460	2.70	13.9
$Lu(OTf)_3$	0.83	461	2.69	15.2
$La(OTf)_3$	0.82	458	2.71	14.4
$Mg(ClO_4)_2$	0.65	451	2.75	12.8
$Ca(ClO_4)_2$	0.58	449	2.76	15.2
$LiClO_4$	0.53	442	2.81	15.0
$Sr(ClO_4)_2$	0.52	445	2.79	13.5
$Ba(ClO_4)_2$	0.49	444	2.79	13.0
$NaClO_4$	0.34	437	2.84	12.8
$Fe(ClO_4)_3$	1.08[b]	478	2.59	13.6
$Fe(ClO_4)_2$	0.96[b]	471	2.63	20.1
$Cu(ClO_4)_2$	0.96[b]	471	2.63	16.9
$Co(ClO_4)_2$	0.95[b]	470	2.64	15.8
$Zn(OTf)_2$	0.71[b]	456	2.72	14.0
$Mn(ClO_4)_2$	0.32[b]	435	2.85	12.8
$(C_6F_5)_2SnBr_2$	0.89	470	2.64	16.8
$(C_6F_5)_3SnBr$	0.65	452	2.74	16.5
Ph_3SnCl	0.62	455	2.72	15.4
Bu_2SnCl_2	0.61	453	2.74	15.6
free	0.32	432	2.87	6.1

[a] Taken from refs 9 and 10a. [b] Calculated from eq 2.

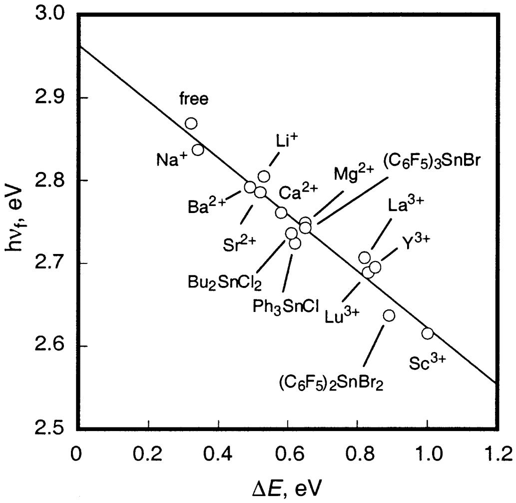

Figure 2. Plot of $h\nu_f$ of the ^{1}AcrCO*−Lewis acid complexes vs ΔE in MeCN 298 K.

Figure 2. The linear correlation between the ΔE values and the $h\nu_f$ values is given by eq 2.

$$\Delta E\ (\mathrm{eV}) = -2.94\ h\nu_f\ (\mathrm{eV}) + 8.70 \qquad (2)$$

The stronger the acidity of the Lewis acid, the larger is the ΔE value, the more red-shifted is the λ_{max} value, and the smaller is the $h\nu_f$ value. It is interesting to note that $Fe(ClO_4)_3$ is stronger Lewis acid than $Sc(OTf)_3$ (Table 1). Such comparison has only been made possible by the present method. The strong Lewis acidity of $(C_6F_5)_2SnBr_2$[12] has also been confirmed quantitatively in this study (Figure 2).

Other aromatic carbonyl compounds such as benzaldehyde (PhCHO) also form complexes with Lewis acids.[11] Although PhCHO is nonfluorescent because of the efficient intersystem crossing, the Lewis acid complex becomes fluorescent.[11] The $h\nu_f$ values of ^{1}PhCHO*−Lewis acid complexes are also well correlated with the ΔE values of the $O_2^{\bullet -}$−Lewis acid complexes (see Supporting Information).

Although antiferromagnetic interaction between paramagnetic Lewis acids and $O_2^{\bullet -}$ have precluded to determine the ΔE values, $h\nu_f$ values of ^{1}AcrCO* complexes with paramagnetic and redox active Lewis acids can be conveniently determined using only a conventional fluorescence spectrophotometer. The good linear correlation between ΔE and $h\nu_f$ in Figure 2 demonstrates that the $h\nu_f$ values provide a quantitative measure of Lewis acidity of all kinds of metal ion salts including paramagnetic and redox active Lewis acids.

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Supporting Information Available: Fluorescence spectra of PhCHO−M^{n+} complexes (S1) and a linear correlation between ΔE and $h\nu_f$ (S2) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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