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Remarkable effects of counter ions on scandium ion-promoted electron transfer reactions

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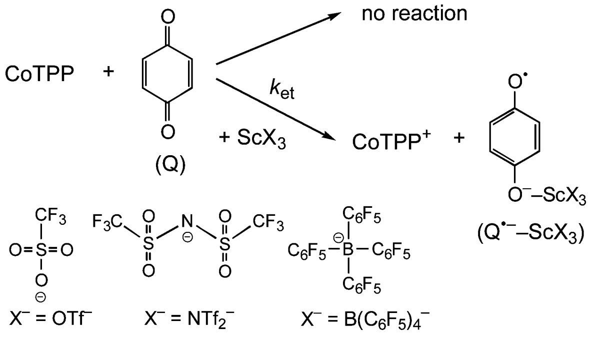
Scandium ion-promoted electron transfer reactions of *p*-benzoquinone are remarkably accelerated when tetrakis(pentafluorophenyl)borate anion is used instead of trifluoromethanesulfonate anion as the counter anion of scandium ion. Only a catalytic amount of scandium borate salt ($Sc[B(C_6F_5)_4]_3$) accelerates significantly the Diels–Alder reaction of 9,10-dimethylanthracene with *p*-benzoquinone, which proceeds via Sc^{3+}-promoted electron transfer from the anthracene to *p*-benzoquinone.

Rare-earth metal triflates acting as strong Lewis acids have attracted considerable attention, since only catalytic amounts of the triflates are required to catalyze a variety of synthetically useful reactions in even aqueous media as well as in many organic solvents.[1] Among rare-earth metal triflates the Lewis acidity of scandium triflate [$Sc(OTf)_3$ (OTf = OSO_2CF_3)] has been reported to be the strongest,[1–4] and $Sc(OTf)_3$ promotes a variety of electron transfer reactions involving electron acceptors, the radical anions of which can bind with Lewis acids most effectively.[2–4] Although a variety of Lewis acids are known to allow Diels–Alder reactions involving carbonyl-containing dienophiles to proceed at room temperature with satisfactory yields, excess amounts of catalysts are normally required to activate the dienophiles.[1,5–7] In contrast, Diels–Alder reactions of various electron deficient dienophiles with dienes have been reported to proceed smoothly in the presence of catalytic amounts of $Sc(OTf)_3$.[1] In this context, we have recently reported that $Sc(OTf)_3$-catalyzed Diels–Alder reaction of anthracenes with *p*-benzoquinone derivatives via $Sc(OTf)_3$-promoted electron transfer from anthracenes to *p*-benzoquinone derivatives.[8] In this case, however, large excess amounts of $Sc(OTf)_3$ are required to complete the reaction.[8] The Lewis acidity of the metal ion is expected to increase with decreasing nucleophilicity of the counter anion. However, the effects of counter anion on the $Sc(OTf)_3$-promoted electron transfer have yet to be examined.

We report herein that Sc^{3+}-promoted electron transfer reactions of *p*-benzoquinone (Q) are remarkably accelerated when tetrakis(pentafluorophenyl)borate anion [$B(C_6F_5)_4^-$][3b] is used instead of triflate anion (OTf^-) or 1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide anion (NTf_2^-)[3b] as the counter anion of scandium ion and that only a catalytic amount of scandium borate salt ($Sc[B(C_6F_5)_4]_3$) accelerates significantly the Diels–Alder reaction of 9,10-dimethylanthracene (DMA) with Q. The difference in the Lewis acidity of ScX_3 with different counter anions (X^-) is shown to be well reflected in the different absorption maxima of the Sc^{3+}-*p*-fluoranil radical anion complex depending on X^-.[9]

No electron transfer from CoTPP (TPP^{2-} = dianion of tetraphenylporphyrin) to Q has occurred in acetonitrile (MeCN) at 298 K.[10] In the presence of ScX_3 (X^- = OTf^-, NTf_2^-, and $B(C_6F_5)_4^-$), however, an efficient electron transfer from CoTPP to Q occurs to yield $CoTPP^+$ and the $Q^{\cdot -}$–ScX_3 complex (Scheme 1). The rates of ScX_3-promoted electron transfer from CoTPP to Q were determined by the UV–vis spectral change for the decay of CoTPP (λ_{max} = 411 nm) as well as the formation of $CoTPP^+$ (λ_{max} = 434 nm) in MeCN at 298 K. The electron transfer rates obeyed second-order kinetics, showing a first-order dependence on concentration of *p*-benzoquinone. The observed second-order rate constant (k_{obs}) for the ScX_3-promoted electron transfer increases linearly with increasing the metal ion concentration (Fig. 1).[11] The ScX_3-promoted electron transfer rate constants (k_{et}) are determined from the slope of the linear plot of k_{obs} *vs.* [ScX_3] as 8.0×10^7, 4.6×10^6 and 2.1×10^6 $dm^6\ mol^{-2}\ s^{-1}$ for X^- = $B(C_6F_5)_4^-$, OTf^- and NTf_2^-, respectively. Thus, the k_{et} value is significantly dependent on the counter ion of Sc^{3+}. The borate anion [$B(C_6F_5)_4^-$], which has the weakest nucleophilicity due to the bulky C_6F_5 groups and the electron withdrawing effect of fluorine,[12] exhibits the highest activity (38 times more active than NTf_2^-) for the ScX_3-promoted electron transfer.



Scheme 1

The $Q^{\cdot -}$–ScX_3 complexes formed in ScX_3-promoted electron transfer from CoTPP to Q (Scheme 1) were too unstable to be detected as the transient absorption spectra even by using a stopped-flow technique.[8] When Q is replaced by *p*-fluoranil (F_4Q), however, the $F_4Q^{\cdot -}$–ScX_3 complex becomes stable enough to be detected spectrophotometrically. The *p*-fluoranil radical anion ($F_4Q^{\cdot -}$) is produced by the electron transfer reduction of F_4Q with decamethylferrocene (Fc^*), since electron transfer from Fc^* (E^0_{ox} *vs.* SCE = −0.08 V)[13] to F_4Q (E^0_{red} *vs.* SCE = −0.04 V)[14] is exergonic. Addition of ScX_3 to the Fc^*–F_4Q system results in formation of the $F_4Q^{\cdot -}$–ScX_3

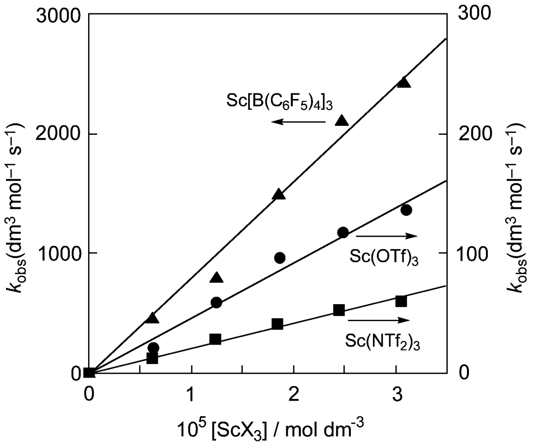


Fig. 1 Plots of k_{obs} *vs.* [ScX_3] for ScX_3-promoted electron transfer from CoTPP to Q in deaerated MeCN at 298 K.

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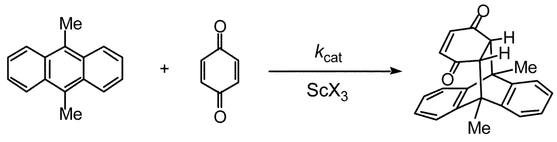
complex as shown in Fig. 2, where the absorption bands due to the $F_4Q^{\cdot-}$–ScX_3 complexes are significantly red-shifted as compared to the absorption band of $F_4Q^{\cdot-}$ (λ_{max} = 431 nm). This indicates that the binding of ScX_3 is stronger in the excited state than the ground state. The λ_{max} values of the $F_4Q^{\cdot-}$–ScX_3 complexes are different depending on X: λ_{max} = 477 and 480 nm for X^- = $B(C_6F_5)_4^-$ and OTf^-, respectively. The absorption spectra of the $F_4Q^{\cdot-}$–metal perchlorate complexes are also measured in the presence of metal perchlorates. The absorption bands of the $F_4Q^{\cdot-}$–metal perchlorate complexes are further red-shifted as the Lewis acidity of metal perchlorates decreases: λ_{max} = 506 nm [$Eu(OTf)_3$], 598 nm [$Ca(ClO_4)_2$], and 618 nm [$Ba(ClO_4)_2$] as shown in Fig. 2. Thus, the weaker the Lewis acidity of metal ion, the more stabilized is the excited state complex than the ground state complex.

Although the reaction of 9,10-dimethylanthracene (DMA) and Q is sluggish in MeCN at 298 K, the addition of ScX_3 results in the efficient [4 + 2] cycloaddition to yield the adduct selectively [eqn. (1)].[8]



(1)

The rates of reactions of ScX_3-catalyzed Diels–Alder reaction of DMA with Q were determined by monitoring the disappearance of absorbance due to DMA (λ_{max} = 398 nm, ε_{max} = 7.5×10^3 dm^3 mol^{-1} cm^{-1}).[8] The rate exhibits second-order kinetics showing a first-order dependence on each reactant concentration. The observed second-order rate constant (k_{obs}) for the ScX_3-catalyzed Diels–Alder reaction increases linearly with increasing ScX_3 concentration (Fig. 3). The ScX_3-catalyzed Diels–Alder reaction rate constants (k_{cat}) are determined from the slope of the linear plot of k_{obs} *vs.* [ScX_3] as 4.9×10^2, 4.8 and 8.0×10^{-1} dm^6 mol^{-2} s^{-1} for X^- = $B(C_6F_5)_4^-$, OTf^-, and NTf_2^- respectively. This order is in agreement with the case of Sc^{3+}-promoted electron transfer from CoTPP to Q (Fig. 1). However, the effect of counter anion on the Diels–Alder reaction is more remarkable than the effect on the ScX_3-promoted electron transfer. The k_{cat} value of $Sc[B(C_6F_5)_4]_3$ is 610 times larger than the value of $Sc(NTf_2)_3$ as compared with the 38 times difference in the corresponding k_{et} values. Such a remarkable catalytic effect of $Sc[B(C_6F_5)_4]_3$ allows the Diels–Alder reaction to proceed smoothly even in the presence of an extremely small concentration of $Sc[B(C_6F_5)_4]_3$ (1.1×10^{-5} mol dm^{-3}) at 298 K, when the rate is 15 times faster than the rate in the absence of the catalyst.

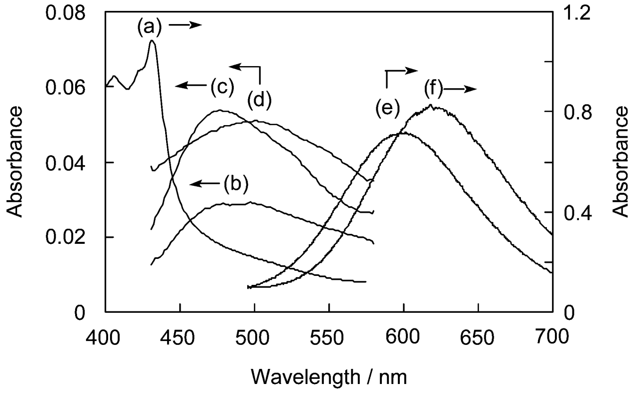


Fig. 2 Electronic absorption spectra observed in electron transfer reduction of (a) F_4Q (5.6×10^{-4} mol dm^{-3}) by Fc* (2.3×10^{-4} mol dm^{-3}) in the absence of metal ion and that of F_4Q (1.1×10^{-3} mol dm^{-3}) by Fc* (4.5×10^{-4} mol dm^{-3}) in the presence of (b) $Sc(OTf)_3$ (1.7×10^{-4} mol dm^{-3}), (c) $Sc[B(C_6F_5)_4]_3$ (5.0×10^{-3} mol dm^{-3}), (d) $Eu(OTf)_3$ (4.7×10^{-3} mol dm^{-3}), (e) $Ca(ClO_4)_2$ (7.3×10^{-3} mol dm^{-3}), and (f) $Ba(ClO_4)_2$ (5.2×10^{-3} mol dm^{-3}) in deaerated MeCN at 298 K.

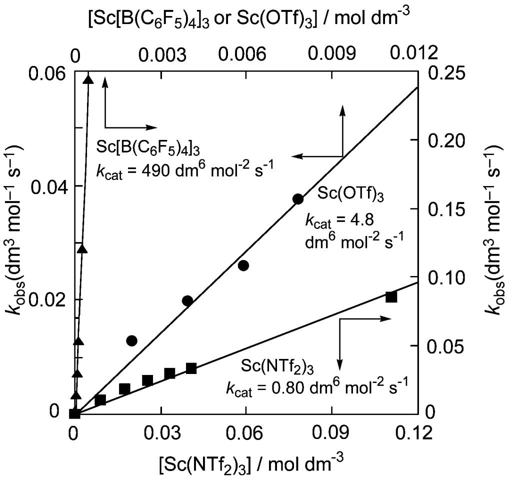


Fig. 3 Plots of k_{obs} *vs.* [ScX_3] for ScX_3-catalyzed Diels–Alder reaction of DMA with Q in deaerated MeCN at 298 K (X^- = OTf^-, $B(C_6F_5)_4^-$, and NTf_2^-).

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