3174 *J. Phys. Chem. A* **2005,** *109,* 3174−3181

Mechanism of Scandium Ion Catalyzed Diels−Alder Reaction of Anthracenes with Methyl Vinyl Ketone

Shunichi Fukuzumi,* Junpei Yuasa, Toshio Miyagawa, and Tomoyoshi Suenobu

Department of Material and Life Science, Graduate School of Engineering, Osaka University, SORST, Japan Science and Technology Corporation (JST), Suita, Osaka 565-0871, Japan

Received: January 19, 2005

Rates of Diels−Alder cycloadditions of anthracenes with methyl vinyl ketone (MVK) are accelerated significantly by the presence of scandium triflate [$Sc(OTf)_3$]. $Sc(OTf)_3$ also promotes photoinduced electron-transfer reactions from various electron donors to MVK significantly. Comparison of the promoting effect of $Sc(OTf)_3$ in photoinduced electron-transfer reactions of MVK with the catalytic effect of $Sc(OTf)_3$ in the Diels−Alder reaction of 9,10-dimethylanthracene with MVK has revealed that the MVK−$Sc(OTf)_3$ complex is a reactive intermediate in both the Diels−Alder and photoinduced electron-transfer reactions. The observed second-order rate constants of the $Sc(OTf)_3$-catalyzed Diels−Alder reactions of anthracenes with MVK are by far larger than those expected from the observed linear Gibbs energy relation for the Diels−Alder reactions of anthracenes with stronger electron acceptors than MVK, which are known to proceed via electron transfer. This indicates that the $Sc(OTf)_3$-catalyzed Diels−Alder reactions of anthracenes with MVK does not proceed via an electron-transfer process from anthracences to the MVK−$Sc(OTf)_3$ complex.

Introduction

The Diels−Alder reaction is one of the most important reactions in the synthesis of natural products and physiologically active molecules.[1] Extensive efforts have been devoted to develop newer methods to improve the yields and selectivities of the [4+2] cycloaddition reactions as well as other cycloadditions.[1−3] The Diels−Alder reaction is generally believed to proceed via a thermally allowed concerted process, governed by one of the Woodword−Hoffmann's rules.[1−4] The Diels−Alder reaction requires opposite electronic features of the substituents at the diene (electron donating) and the dienophile (electron withdrawing) ends for the reaction to be reasonably fast.[4−6] Unsymmetrical substitution often favors an asynchronous concerted mechanism including biradicaloid transition states or stepwise processes, whereas Diels−Alder reactions of symmetrical addends usually involve synchronous C−C bond formation.[4−7] On the other hand, there have recently been increasing interests in the important role of electron-transfer processes as the activation step for some Diels−Alder reactions of electron-rich dienes with high-lying HOMO with electron-deficient dienophiles with low-lying LUMO.[8,9] Since the photoexcitation results in a significant change in the HOMO or LUMO level, photoinduced electron transfer between dienes and dienophiles leads to the Diels−Alder reaction which is thermally inaccessible.[10−13] The LUMO level of dienophiles can also be decreased by complexation with Lewis acids and thus, Lewis acid catalyzed Diels−Alder reaction has extensively been studied because of the broad utility in total synthesis, becoming a classic reaction for the evaluation of new chiral Lewis acids.[1−3,14−19] The decrease in the LUMO level of dienophiles is expected to enhance the concerted reactivity in the Diels−Alder reaction, because of the stronger HOMO−LUMO interaction. At the same time, the electron-transfer reactivity of the dienophile, which can act as an electron acceptor, is also enhanced by the complexation of the dienophile with Lewis acids.[20,21] Such mechanistic dichotomy, i.e., the role of electron transfer has been clarified in Diels−Alder reaction of anthracenes with *p*-benzoquinone (Q), catalyzed by metal ions acting as Lewis acids,[22] which has provided the experimental proof of the electron-transfer mechanism of metal ion catalyzed Diels−Alder reaction.[22]

In the case of relatively strong electron acceptors such as Q, metal ions can form complexes only with the one-electron reduced species ($Q^{\bullet-}$) whereas Q itself is not basic enough to form the complex with metal ions which act as Lewis acids.[22] When Q is replaced by a dienophile which is a much weaker electron acceptor than Q, the dienophile can form the metal ion complex, which may react directly with a diene via an enhanced concerted pathway. From the viewpoint of developing newer methods to improve the yields and selectivities of the Diels−Alder reaction, it is important to clarify the mechanism of metal ion catalyzed Diels−Alder reaction when metal ion can form a complex with a dienophile. With regard to the existing uncertainty concerning this dichotomy, important questions arise: What are the factors that determine whether metal ion catalyzed Diels−Alder reaction proceeds via an electron transfer or a concerted (synchronous or asynchronous) pathway? However, such a mechanistic dichotomy has yet to be clarified for Diels−Alder reactions of metal ion complexes of dienophiles.

We report herein that Diels−Alder reactions of anthracenes with methyl vinyl ketone (MVK), which can form 1:1 complex with Sc^{3+}, proceed efficiently via a scandium triflate [$Sc(OTf)_3$]-catalyzed process. The catalytic effects of Sc^{3+} salts in the Diels−Alder reaction of MVK are fully compared with the promoting effects of Sc^{3+} salts in photoinduced electron-transfer reactions. The direct spectroscopic detection of complexes formed between the radical anion of MVK and $Sc(OTf)_3$, combined with the detailed kinetic analysis of the catalytic

---

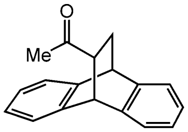
* To whom correspondence should be addressed. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp.

10.1021/jp050347u CCC: $30.25

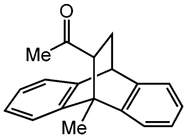
TABLE 1: Yields of Products in Diels−Alder Reactions of Anthracene Derivatives with MVK in the Absence and Presence of $Sc(OTf)_3$ (2.0×10^{-2} M) in CD_3CN at 343 K

anthracene derivative	$[Sc(OTf)_3]$ (M)	time	product	yield[a] (%)	selectivity
anthracene	2.0×10^{-2}	120 days	**1**	100	
9-methylanthracene	2.0×10^{-2}	60 min	**2a**	100	100 (**2a**):0 (**2b**)
	0	21 days	**2a** and **2b**	40	75 (**2a**):25 (**2b**)
9,10-dimethylanthracene	2.0×10^{-2}	60 min	**3**	100	
9-ethylanthracene	2.0×10^{-2}	60 min	**4a** and **4b**	85	82 (**4a**):18 (**4b**)
	0	14 days	**4a** and **4b**	26	77 (**4a**):23 (**4b**)
9-benzylanthracene	2.0×10^{-2}	90 min	**5a** and **5b**	93	97 (**5a**):3 (**5b**)
	0	14 days	**5a** and **5b**	4	75 (**5a**):25 (**5b**)

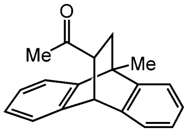
[a] Determined by 400-MHz ^1H NMR spectra.



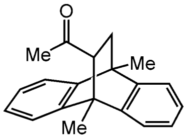
(1)



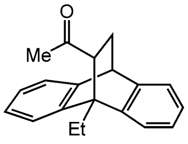
(2a)



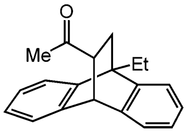
(2b)



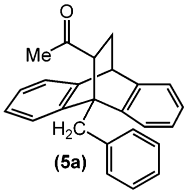
(3)



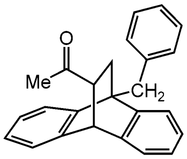
(4a)



(4b)



(5a)



(5b)

effects of Sc^{3+} salts on the Diels−Alder reactions and the promoting effects of Sc^{3+} salts on electron-transfer reactions of MVK provides a confirmative basis to delineate the catalytic mechanism of Sc^{3+} salts in the Diels−Alder reaction.

Results and Discussion

Effects of Scandium Ion on Diels−Alder and Electron-Transfer Reactions of Methyl Vinyl Ketone. No reaction of 9,10-dimethylanthracene (DMA) with methyl vinyl ketone (MVK) occurred in MeCN at 298 K. However, addition of $Sc(OTf)_3$ (2.0×10^{-2} M) to the DMA−MVK system results in the efficient [4+2] cycloaddition to yield the adduct selectively. The [4+2] cycloaddition of anthracene, 9-methylanthracene, 9-ethylanthracene, and 9-benzylanthracene with MVK also occurs efficiently in the presence of $Sc(OTf)_3$ to yield the corresponding adducts. The product yields in the absence and presence of $Sc(OTf)_3$ are listed in Table 1. In the absence of $Sc(OTf)_3$, the Diels−Alder reaction of 9-methylanthracene occurs at a high temperature 343 K, when two regioisomers (**2a** and **2b**) were obtained in 3:1 ratio. In the presence of $Sc(OTf)_3$ (2.0×10^{-2} M), however, the reaction occurs much more efficiently at 343 K, when only one regioisomer (**2a**) was obtained selectively.[23] The regioselectivity (**4a** vs **4b** or **5a** vs **5b**) is also improved in the presence of $Sc(OTf)_3$ in the case of 9-ethylanthracene and 9-benzylanthracene (Table 1).

The rates of Diels−Alder reaction of DMA with MVK in the presence of $Sc(OTf)_3$ (2.0×10^{-2} M) in MeCN at 298 K were determined by monitoring the disappearance of absorbance due to DMA ($\lambda_{max} = 398$ nm, $\epsilon_{max} = 7.5 \times 10^3$ M^{-1} cm^{-1}) as shown in Figure 1. The rates obeyed pseudo-first-order kinetics in the presence of large excess MVK and $Sc(OTf)_3$ relative to the concentration of DMA.

The rate of Diels−Alder reaction becomes 31 times faster when tetrakis(pentafluorophenyl)borate anion $[B(C_6F_5)_4^-]$[24] is used instead of triflate anion (OTf^-) as the counteranion (X^-) of scandium ion under the same experimental conditions ([MVK] = 3.0×10^{-2} M, $Sc(X)_3 = 2.0 \times 10^{-2}$ M, [DMA] = 2.2×10^{-4} M); see inset of Figure 1.

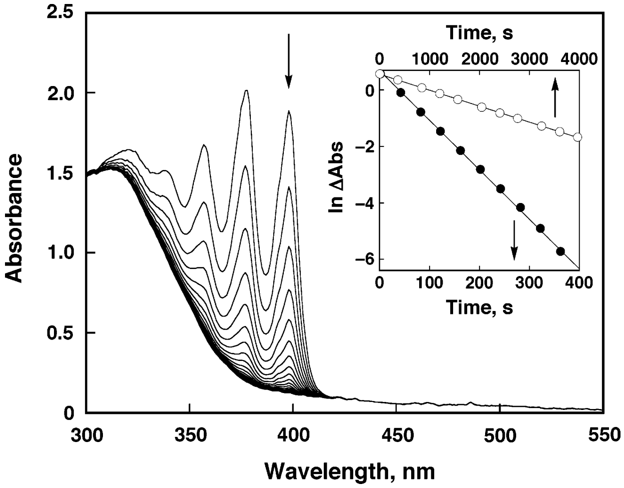


Figure 1. Spectral changes observed in the Diels−Alder reaction of 9,10-dimethylanthracene (2.2×10^{-4} M) with MVK (3.0×10^{-2} M) in the presence of $Sc(OTf)_3$ (2.0×10^{-2} M) in deaerated MeCN at 298 K. Inset: First-order plots in Diels−Alder reaction of 9,10-dimethylanthracene (2.2×10^{-4} M) with MVK (3.0×10^{-2} M) in the presence of $Sc(OTf)_3$ (○, 2.0×10^{-2} M) and $Sc[B(C_6F_5)_4]_3$ (●, 2.0×10^{-2} M) in deaerated MeCN at 298 K.

The pseudo-first-order rate constants ($k_{(1)}$) of the Diels−Alder reactions of the other anthracenes also increase proportionally with MVK concentration (see Supporting Information S2). The second-order rate constants (k_{obs}) were determined from the slopes of the linear relations between $k_{(1)}$ and MVK concentration. The dependence of k_{obs} on $[Sc(OTf)_3]$ was examined for Diels−Alder reaction of DMA with MVK at various concentrations of $Sc(OTf)_3$. The results are shown in Figure 2a, where the k_{obs} value increases with increasing $Sc(OTf)_3$ concentration to approach a limited value. The k_{obs} value also increases with increasing $Sc[B(C_6F_5)_4]_3$ concentration, which is more than 10 times larger than the case of $Sc(OTf)_3$ at a low concentration region (Figure 2b).[25]

$Sc(OTf)_3$ also promotes photoinduced electron transfer from various electron donors to MVK. No emission quenching of

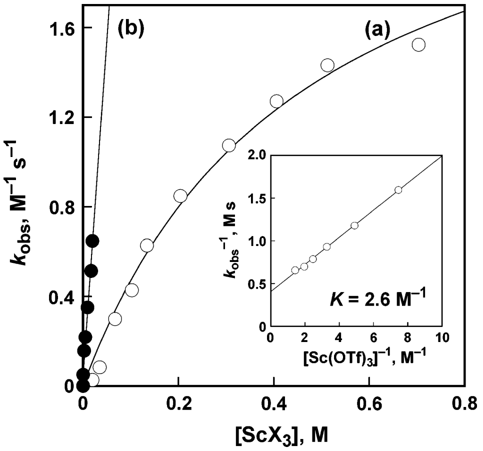


Figure 2. Dependence of k_{obs} on (a) [Sc(OTf)$_3$] (○) and (b) [Sc-[B(C$_6$F$_5$)$_4$]$_3$] (●) for the Diels−Alder reaction of 9,10-dimethylanthracene (1.0×10^{-4} M) with MVK in the presence of ScX$_3$ (X = OTf and B(C$_6$F$_5$)$_4$) in deaerated MeCN at 298 K. Inset: Plot of k_{obs}^{-1} vs [Sc(OTf)$_3$]$^{-1}$.

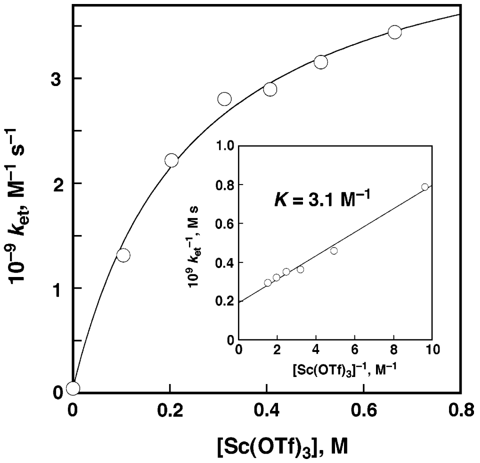


Figure 3. Dependence of k_{et} on [Sc(OTf)$_3$] for the fluorescence quenching of 9-cyanoanthracene (9.8×10^{-5} M) by MVK in the presence of Sc(OTf)$_3$ in deaereted MeCN at 298 K. Inset: Plot of k_{et}^{-1} vs [Sc(OTf)$_3$]$^{-1}$.

Ru(bpy)$_3^{2+}$ by MVK was observed in MeCN. However, addition of Sc(OTf)$_3$ to an MeCN solution of Ru(bpy)$_3^{2+}$ and MVK results in efficient quenching of the Ru(bpy)$_3^{2+}$ emission. The fluorescence quenching of anthracenes (anthracene, 9-methylanthracene, 9,10-dibromoanthracene, and 9-cyanoanthracene) by MVK are also promoted by Sc(OTf)$_3$ (see Supporting Information S3,4). The rate constants of photoinduced electron transfer (k_{et}) were determined from slopes of Stern−Volmer plots and the fluorescence lifetimes (see Supporting Information and Experimental Section). The saturated dependence of the photoinduced electron-transfer rate constants (k_{et}) on [Sc(OTf)$_3$] is also observed as shown in Figure 3.

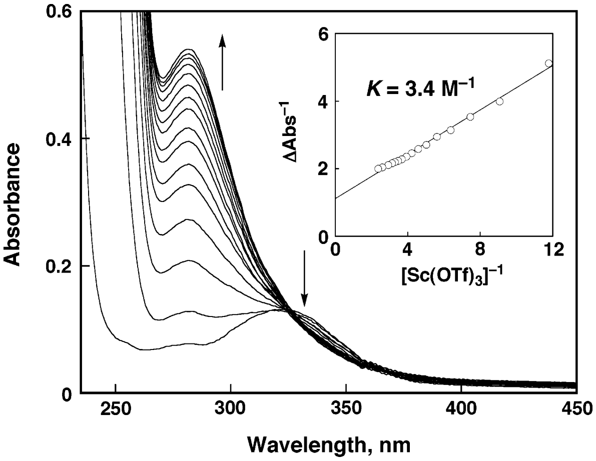


Figure 4. UV−visible absorption spectra of MVK (2.1×10^{-2} M) in the presence of various concentrations of Sc(OTf)$_3$ (0 to 4.2×10^{-1} M) in MeCN at 298 K (2 mm path length). Inset: Plot of ΔAbs^{-1} at 283 nm vs [Sc(OTf)$_3$]$^{-1}$.

TABLE 2: Observed Second-Order Rate Constant (k^0_{obs}) of Sc(OTf)$_3$-Promoted Diels−Alder Reaction of 9,10-Dimethylanthracene with the MVK−Sc(OTf)$_3$ Complex, Electron Transfer Rate Constant (k^0_{et}) of Fluorescence Quenching of 9-Cyanoanthracene by the MVK−Sc(OTf)$_3$ Complex, and Formation Constant of the MVK−Sc(OTf)$_3$ Complex (K) in Deaerated MeCN at 298 K

electron donor	k^0_{obs} and k^0_{et}[a] (M^{-1} s^{-1})	K[a] (M^{-1})
9,10-dimethylanthracene	2.5	2.6
9-cyanoanthracene	5.2×10^9	3.1

[a] Determined from the dependence of k_{obs} or k_{et} on [Sc(OTf)$_3$] based on eq 4. The experimental error is ±10%.

The saturated dependence of k_{obs} (Figure 2a) and k_{et} (Figure 3) with respect to concentration of Sc(OTf)$_3$ results from the 1:1 complex formation between MVK and Sc(OTf)$_3$, which enhances the elecrophilic and electron acceptor ability of MVK to accelerate the Diels−Alder and photoinduced electron-transfer reactions as shown in Scheme 1. Such 1:1 complex formation between MVK and Sc(OTf)$_3$ is confirmed by a UV−vis spectral change of MVK in the presence of various concentrations of Sc(OTf)$_3$ as shown in Figure 4. Such an absorbance change due to the complex formation is expressed by eq 1, which is rewritten by eq 2, where A_0 and A_∞ are absorbance at 282 nm due to MVK and absorbance due to the MVK−Sc(OTf)$_3$ complex, respectively. The formation constant (K) is obtained

$$A - A_0 = K[\mathrm{Sc(OTf)_3}](A_\infty - A_0)/(1 + K[\mathrm{Sc(OTf)_3}]) \quad (1)$$

$$(A - A_0)^{-1} = (A_\infty - A_0)^{-1} + \{K[\mathrm{Sc(OTf)_3}](A_\infty - A_0)\}^{-1} \quad (2)$$

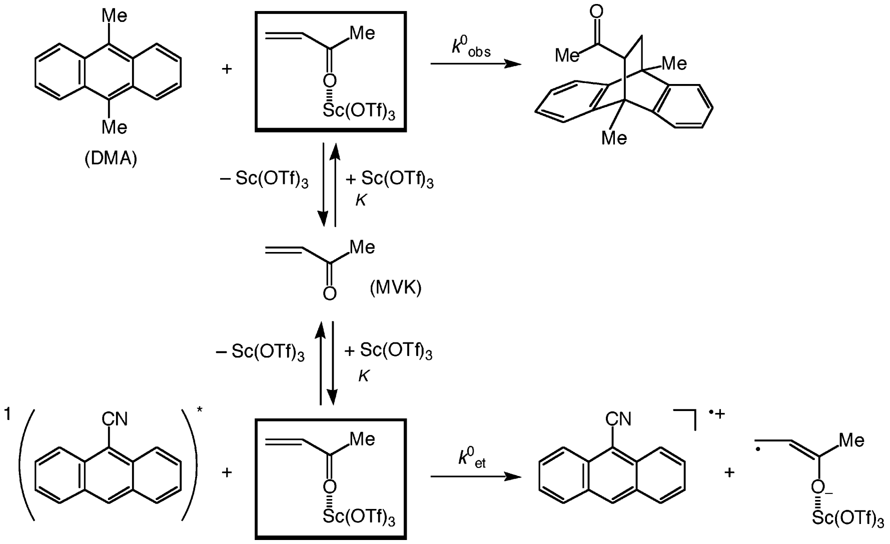
as 3.4 M^{-1} from a linear plot of $(A - A_0)^{-1}$ (= ΔAbs^{-1}) vs [Sc(OTf)$_3$]$^{-1}$ (see inset of Figure 4). If both the Diels−Alder and photoinduced electron-transfer reactions proceed via the MVK−Sc(OTf)$_3$ complex (Scheme 1), the dependence of second-order rate constant of Diels−Alder reaction (k_{obs}) and the fluorescence quenching rate constant (k_{et}) is expressed by eq 3, which is rewritten by a linear relation between k_{obs}^{-1} (or k_{et}^{-1}) and [Sc(OTf)$_3$]$^{-1}$ (eq 4). From the slopes and intercepts

$$k_{obs}\ (\text{or } k_{et}) = k^0_{obs}(\text{or } k^0_{et})K[\mathrm{Sc(OTf)_3}]/(1 + K[\mathrm{Sc(OTf)_3}]) \quad (3)$$

$$k_{obs}^{-1}\ (\text{or } k_{et}^{-1}) = \{k^0_{obs}(\text{or } k^0_{et})K[\mathrm{Sc(OTf)_3}]\}^{-1} + k^{0\,-1}_{obs}(\text{or } k^{0\,-1}_{et}) \quad (4)$$

of linear plots of k_{obs}^{-1} vs [Sc(OTf)$_3$]$^{-1}$ (inset of Figure 2) and k_{et}^{-1} vs [Sc(OTf)$_3$]$^{-1}$ (inset of Figure 3) are obtained the K values which are listed in Table 2 together with the k^0_{obs} and k^0_{et} values. These K values derived from Sc(OTf)$_3$-catalyzed Diels−Alder reaction (K = 2.6 M^{-1}) and the electron transfer (K = 3.1 M^{-1}) agree with that determined from UV−vis spectral change of MVK in the presence of various concentrations of Sc(OTf)$_3$ (K = 3.4 M^{-1}). Such agreement indicates that the MVK−Sc(OTf)$_3$ complex is a common reactive intermediate in both reactions.

SCHEME 1



Large Positive Shift in the One-Electron Reduction Potential of MVK Due to the Complex Formation with Sc(OTf)$_3$. Since direct electrochemical measurements of MVK were complicated by the irreversible behavior upon the one-electron reduction, we have examined rates of outer-sphere electron-transfer reduction of MVK in the absence and in the presence of 5.0×10^{-1} M Sc(OTf)$_3$,[26] from which the one-electron reduction potentials can be deduced (vide infra). A large positive shift in the one-electron reduction potential of MVK in the presence of 5.0×10^{-1} M Sc(OTf)$_3$ as compared with that of MVK in the absence of Sc(OTf)$_3$ is estimated by comparing the electron-transfer rate constants of photoinduced electron-transfer reduction of MVK in the presence of 5.0×10^{-1} M Sc(OTf)$_3$ with those in the absence of Sc(OTf)$_3$ in MeCN at 298 K. The k_{et} value of the emission quenching by photoinduced electron transfer is obtained by eq 5, where Z is the collision frequency, taken as 1×10^{11} M^{-1} s^{-1}, $\Delta G^{\ddagger}$ is the

$$1/k_{et} = 1/\{Z \exp[-(\Delta G^{\ddagger}/k_BT)]\} + 1/k_{diff} \qquad (5)$$

activation free energy of the bimolecular electron-transfer process, k_B is the Boltzmann constant, and k_{diff} is the diffusion rate constant which is taken as 2×10^{10} M^{-1} s^{-1} in MeCN.[27,28] The dependence of $\Delta G^{\ddagger}$ on the free energy change of electron transfer (ΔG_{et} in eV) has well been established as given by eq 6, where $\Delta G^{\ddagger}_0$ is the intrinsic barrier that represents the

$$\Delta G^{\ddagger} = (\Delta G_{et}/2) + [(\Delta G_{et}/2)^2 + (\Delta G^{\ddagger}_0)^2]^{1/2} \qquad (6)$$

activation Gibbs energy when the driving force of electron transfer is zero, that is, $\Delta G^{\ddagger} = \Delta G^{\ddagger}_0$ at $\Delta G_{et} = 0$.[27] On the other hand, the ΔG_{et} values are obtained from the one-electron oxidation potential of the excited state of donors (E_{ox}) and the one-electron reduction potential of the acceptors (E_{red}) by using eq 7, where e is the elementary charge.[27−29] From eqs 6 and 7 is derived a linear relation between $E_{ox} - (\Delta G^{\ddagger}/e)$ and $(\Delta G^{\ddagger})^{-1}$

$$\Delta G_{et} = e(E_{ox} - E_{red}) \qquad (7)$$

as shown in eq 8.[28] The $\Delta G^{\ddagger}$ values are obtained from the photoinduced electron transfer rate constants (k_{et}) of electron

$$E_{ox} - (\Delta G^{\ddagger}/e) = E_{red} - (\Delta G^{\ddagger}_0/e)^2/(\Delta G^{\ddagger}/e) \qquad (8)$$

transfer from excited donors to acceptors using eq 5. We can choose appropriate electron donors whose E_{ox} values are known or readily determined. Thus, the unknown values of E_{red} and $\Delta G^{\ddagger}_0$ can be determined from the intercept and slope of the linear plots of $E_{ox} - (\Delta G^{\ddagger}/e)$ vs $(\Delta G^{\ddagger}/e)^{-1}$ using eq 8.

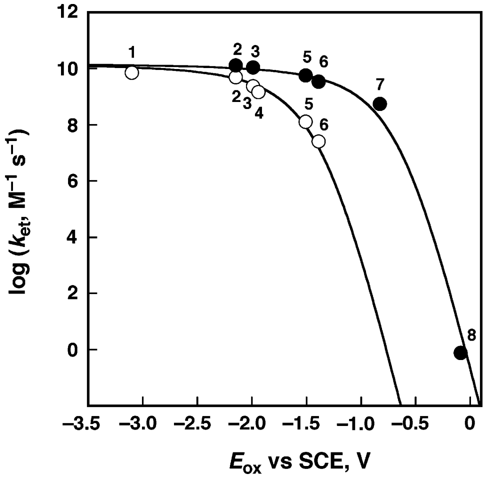


Figure 5. Plots of log k_{et} vs E_{ox} for electron transfer from the excited states and ground state of various donors to MVK in the absence of Sc(OTf)$_3$ (○) and in the presence of 5.0×10^{-1} M Sc(OTf)$_3$ (●) in deaerated MeCN at 298 K. Numbers correspond to electron donors in Table 3.

A number of k_{et} values of photoinduced electron transfer from the singlet excited states of electron donors and the excited state of Ru(bpy)$_3^{2+}$ to MVK in the absence of Sc(OTf)$_3$ and in the presence of 5.0×10^{-1} M Sc(OTf)$_3$ were determined from fluorescence quenching by MVK. The results are summarized in Table 3 together with the one-electron oxidation potentials (E_{ox}) of electron donors examined in this study. The E_{ox}* values of the excited states are obtained by subtracting the 0,0-excitation energies ($\Delta E_{0,0}$) from the one-electron oxidation potentials in the ground states (E_{ox}).[30,31]

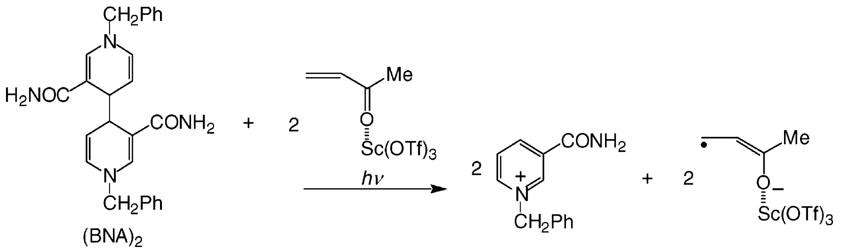
Figure 5 shows plots of log k_{et} vs E_{ox} for photoinduced electron transfer from the excited states of various electron donors and thermal electron transfer from electron donors to MVK in the absence and the presence of Sc(OTf)$_3$ (5.0×10^{-1} M) in MeCN at 298 K. In both cases the log k_{et} values increase with decrease in the E_{ox} value to reach a diffusion-limited value.[32] The E_{red} value of MVK (−1.32 V vs SCE) and that in

TABLE 3: Rate Constants (k_{et}) of Electron Transfer from Electron Donors to MVK and the MVK−Sc(OTf)$_3$ Complex in the Absence and Presence of Sc(OTf)$_3$ (5.0×10^{-1} M) in Deaerated MeCN at 298 K and One-Electron Oxidation Potentials of Electron Donors (E_{ox}), Excitation Energies ($\Delta E_{0,0}$) and One-Electron Oxidation Potentials (E_{ox}*) of Singlet Excited States of Electron Donors in MeCN at 298 K

no.	electron donor[a]	E_{ox} (V vs SCE)	$\Delta E_{0,0}$[b] (eV)	E_{ox}*[c] (V vs SCE)	in the absence of Sc(OTf)$_3$ k_{et}[d] (M^{-1} s^{-1})	in the presence of 5.0×10^{-1} M Sc(OTf)$_3$ k_{et} (M^{-1} s^{-1})
1	10-methyl-9,10-dihydroacridine*	0.80	3.90	−3.10	7.2×10^9	
2	anthracene*	1.19	3.34	−2.15	5.0×10^9	$1.3 \times 10^{10,f}$
3	9-methylanthracene*	1.11	3.10	−1.99	2.4×10^9	$1.1 \times 10^{10,f}$
4	9,10-dimethylanthracene*	1.05	2.99	−1.94	1.5×10^9	*g*
5	9,10-dibromoanthracene*	1.42	2.93	−1.51	1.3×10^8	$5.7 \times 10^{9,f}$
6	9-cyanoanthracene*	1.55	2.94	−1.39	2.6×10^7	$3.4 \times 10^{9,f}$
7	Ru(bpy)$_3$(Cl)$_2$*	1.29	2.12	−0.83	*e*	$5.6 \times 10^{8,f}$
8	Decamethylferrocene	−0.08			n.r.	7.7×10^{-1}

[a] The asterisk (*) denotes the excited state. [b] Determined from the absorption maxima and emission maxima in MeCN. [c] Obtained by subtracting the $\Delta E_{0,0}$ values from the E_{ox} values. [d] Determined from the Stern−Volmer plots for the fluorescence quenching. [e] No emission quenching in the absence of Sc(OTf)$_3$. [f] Determined from the K_{sv}/τ values. [g] Cannot be determined because thermal Diels−Alder reaction is too fast to examine the fluorescence quenching experiment under these conditions.

SCHEME 2



the presence of 5.0×10^{-1} M Sc(OTf)$_3$ (−0.60 V vs SCE) as well as the $\Delta G^{\ddagger}_0$ value of MVK (0.26 eV) and that in the presence of 5.0×10^{-1} M Sc(OTf)$_3$ (0.25 eV) were determined from the intercepts and slopes of the linear plots of $E_{ox} - (\Delta G^{\ddagger}/e)$ vs $(\Delta G^{\ddagger}/e)^{-1}$ using eq 8 (see Supporting Information S5).[31] The plots of Figure 5 are fitted using the E_{red} and $\Delta G^{\ddagger}_0$ values as shown by solid line, which agrees well with the experimental results. As compared to the E_{red} value of MVK in the absence of Sc(OTf)$_3$, the E_{red} value in the presence of 5.0×10^{-1} M Sc(OTf)$_3$ is significantly shifted to the positive direction (+0.72 V). Such a large positive shift in the one-electron reduction potential indicates that the electron acceptor ability of MVK is dramatically enhanced by the complex formation with Sc(OTf)$_3$.

Electron Spin Resonance (ESR) Detection of the MVK$^{\bullet -}$−Sc(OTf)$_3$ Complex. The one-electron reduction of the MVK−Sc(OTf)$_3$ complex results in formation of the corresponding radical anion complex, MVK$^{\bullet -}$−Sc(OTf)$_3$. Although the MVK$^{\bullet -}$−Sc(OTf)$_3$ complex is too unstable to be detected by ESR at 298 K, the ESR spectrum has been detected successfully by utilizing photoinduced electron transfer from the dimeric *N*-benzyldihydronicotinamide [(BNA)$_2$] to MVK in the presence of Sc(OTf)$_3$ in butyronitrile at low temperatures. Irradiation of a butyronitrile solution containing (BNA)$_2$ (2.0×10^{-2} M), MVK (6.1×10^{-1} M), and Sc(OTf)$_3$ (5.0×10^{-1} M) with a mercury lamp at 203 K results in formation of MVK$^{\bullet -}$−Sc(OTf)$_3$ by photoinduced electron transfer from the singlet excited state of (BNA)$_2$ to MVK followed by a fast cleavage of the C−C bond of the dimer and a second electron transfer to MVK (Scheme 2).[32] The ESR spectrum thus obtained for the MVK$^{\bullet -}$−Sc(OTf)$_3$ complex is shown in Figure 6 together with the computer simulation spectrum. The broad triplet ESR signal indicates that two equivalent protons have a large *hfc* value of 23 G. This indicates that the unpaired electron is localized largely on the γ-carbon and that the negative charge is mainly located on the oxygen atom of MVK, to which one Sc(OTf)$_3$ binds as shown in Figure 6.[33]

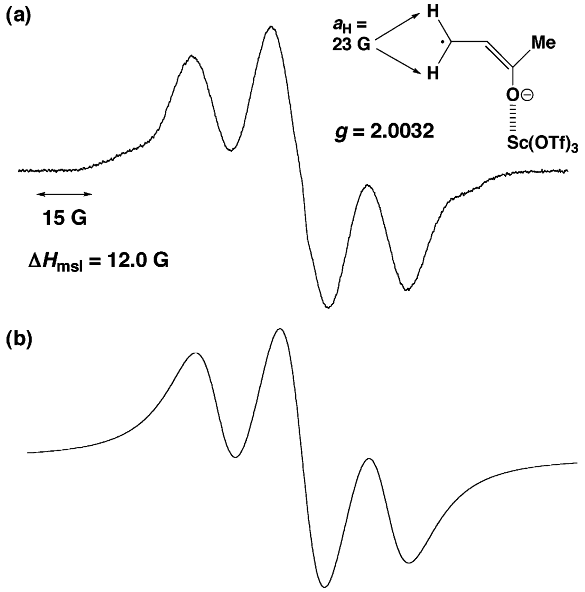


Figure 6. ESR spectrum of a butyronitrile solution containing (BNA)$_2$ (2.0×10^{-2} M) and MVK (6.1×10^{-1} M) in the presence of Sc(OTf)$_3$ (5.0×10^{-1} M) observed under photoirradiation with a high-pressure mercury lamp at 203 K.

Mechanism of Scandium Ion Catalyzed Diels−Alder Reaction of Anthracenes with Methyl Vinyl Ketone. The free energy change of electron transfer (ΔG_{et}) from anthracenes to MVK in the presence of 5.0×10^{-1} M Sc(OTf)$_3$, to Q in the presence of Mg(ClO$_4$)$_2$ (1.6 M) and also to tetracyanoethylene (TCNE) can be evaluated from the difference in the oxidation potentials of anthracenes and the reduction potentials of the electron acceptors.[34,35] The k_{obs} values for the Diels−Alder reactions of anthracenes with MVK in the presence of Sc(OTf)$_3$ (5.0×10^{-1} M), Q in the presence of Mg(ClO$_4$)$_2$ (1.6 M), and

TABLE 4: Rate Constants (k_{obs}) of Diels−Alder Reactions of Anthracenes with TCNE, Q in the Presence of $Mg(ClO_4)_2$ (1.6 M), and MVK in the Presence of $Sc(OTf)_3$ (5.0×10^{-1} M) in Deaerated MeCN at 298 K, One-Electron Oxidation Potentials (E_{ox}) of Anthracenes and One-Electron Reduction Potentials (E_{red}) of TCNE, Q in the Presence of $Mg(ClO_4)_2$ (1.6 M), and MVK in the Presence of $Sc(OTf)_3$ (5.0×10^{-1} M) in MeCN at 298 K, and Free Energy Change of Electron Transfer (ΔG_{et}) from Anthracenes to TCNE, Q in the Presence of $Mg(ClO_4)_2$ (1.6 M), and MVK in the Presence of $Sc(OTf)_3$ (5.0×10^{-1} M) in MeCN at 298 K

no.	electron donor	electron acceptor	metal ion salt	E_{ox}[b] (V vs SCE)	E_{red} (V vs SCE)	ΔG_{et} (eV)	k_{obs} (M^{-1} s^{-1})
1	9-methylanthracene	TCNE	*a*	1.11	0.22[c]	0.89	1.1×10^3
2	anthracene	TCNE	*a*	1.19	0.22[c]	0.97	3.3
3	9-bromoanthracene	TCNE	*a*	1.30	0.22[c]	1.08	3.1×10^{-1}
4	9,10-dimethylanthracene	Q	$Mg(ClO_4)_2$	1.05	−0.01[d]	1.06	5.0×10^{-2}
5	9-methylanthracene	Q	$Mg(ClO_4)_2$	1.11	−0.01[d]	1.12	2.5×10^{-3}
6	anthracene	Q	$Mg(ClO_4)_2$	1.19	−0.01[d]	1.20	2.6×10^{-5}
7	9-benzylanthracene	Q	$Mg(ClO_4)_2$	1.20	−0.01[d]	1.21	2.1×10^{-4}
8	9-bromoanthracene	Q	$Mg(ClO_4)_2$	1.30	−0.01[d]	1.31	6.7×10^{-6}
9	9,10-dimethylanthracene	MVK	$Sc(OTf)_3$	1.05	−0.60	1.65	1.4
10	9-methylanthracene	MVK	$Sc(OTf)_3$	1.11	−0.60	1.71	4.0×10^{-1}
11	anthracene	MVK	$Sc(OTf)_3$	1.19	−0.60	1.79	9.2×10^{-3}
12	9-benzylanthracene	MVK	$Sc(OTf)_3$	1.20	−0.60	1.80	4.3×10^{-2}
13	9-bromoanthracene	MVK	$Sc(OTf)_3$	1.30	−0.60	1.90	1.9×10^{-3}

[a] In the absence of metal ion. [b] Taken from ref 22a. [c] Taken from ref 35. [d] Taken from ref 34.

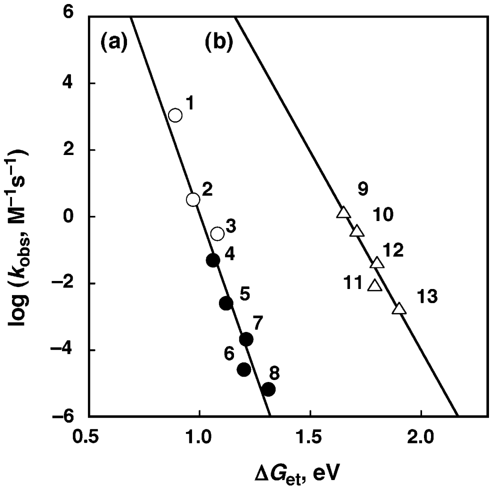


Figure 7. Plots of log k_{obs} vs ΔG_{et} for the Diels−Alder reaction of anthracenes with (a) TCNE (○), Q in the presence of 1.6 M $Mg(ClO_4)_2$ (●), and (b) MVK in the presence of 5.0×10^{-1} M $Sc(OTf)_3$ (△) in deaerated MeCN at 298 K. Numbers refer to those in Table 4.

TCNE in MeCN at 298 K are listed in Table 4 together with the E_{ox} values of anthracenes.[8a,22]

Plots of log k_{obs} vs ΔG_{et} for the Diels−Alder reactions of anthracenes with MVK in the presence of $Sc(OTf)_3$ (5.0×10^{-1} M), Q in the presence of $Mg(ClO_4)_2$ (1.6 M), and TCNE are shown together in Figure 7. First, it should be noted that the Diels−Alder reactions of anthracenes with two different dienophiles, Q in the presence of $Mg(ClO_4)_2$ (1.6 M) and TCNE, have a single correlation. Such a single correlation between log k_{obs} vs ΔG_{et} has been well understood in terms of the electron-transfer mechanism. The general scheme for an electron-transfer process from an electron donor (D) to an acceptor (A) in the donor−acceptor complex formed between D and A, followed by facile bond formation between $D^{\bullet +}$ and $A^{\bullet -}$ to afford the Diels−Alder adduct (D−A) is represented by eq 9, in which electron transfer in the donor−acceptor complex is rate-limiting.

$$D + A \overset{K_{DA}}{\rightleftharpoons} [DA] \xrightarrow{k_{ET}} [D^{\bullet +}A^{\bullet -}] \xrightarrow{\text{fast}} D{-}A \qquad (9)$$

When the electron transfer is endergonic (i.e., $\Delta G_{et} > 0$), the observed second-order rate constant k_{obs} is given by eq 10, where K_{DA} is the formation constant of the donor−acceptor complex

$$k_{obs} = k_{ET}K_{DA} \qquad (10)$$

and k_{ET} is the rate constant of intracomplex electron transfer. In a highly endergonic region, the activation Gibbs energy for electron transfer $\Delta G^{\ddagger}_{ET}$ in the complex is approximately equal to the free energy change of intracomplex electron transfer and, thus, is given by eq 11, where w_p and w_r represent the energy required to bring together the products and reactants to within

$$\Delta G^{\ddagger}_{ET} = \Delta G_{et} + w_p - w_r \qquad (11)$$

the donor−acceptor complex, respectively. The observed second-order rate constant (k_{obs}) in eq 11 can be expressed in terms of $\Delta G^{\ddagger}_{ET}$ and w_r as eq 12, where Z is the collision frequency. The combination of eqs 11 and 12 affords the linear Gibbs energy

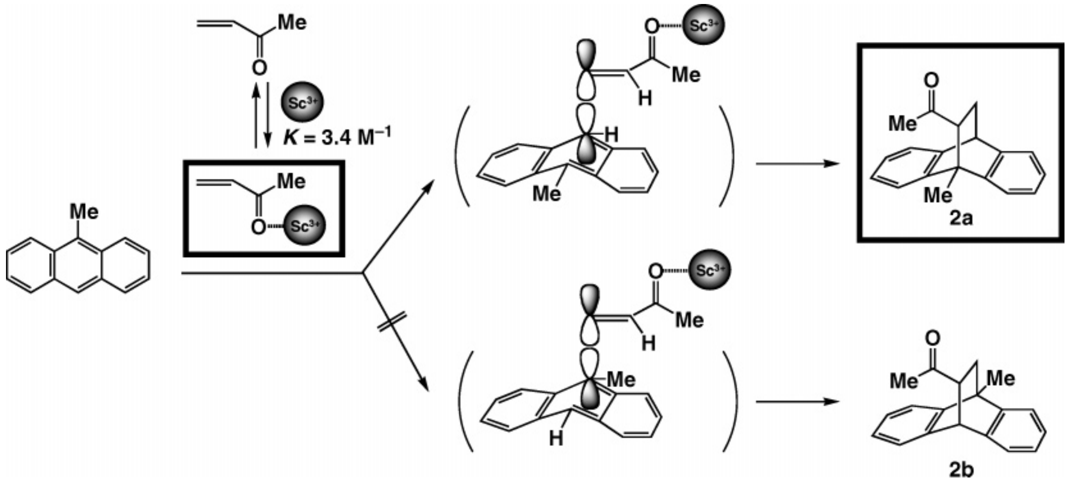
$$k_{obs} = Z \exp[-(\Delta G^{\ddagger}_{ET} + w_r)/RT] \qquad (12)$$

relation between log k_{obs} and ΔG_{et} in eq 13, which agrees with the experimental single linear correlation between log k_{obs} and ΔG_{et} for the Diels−Alder reactions of anthracenes with two

$$\log k_{obs} = -(\Delta G_{et} + w_p)/(2.3RT) + \log Z \qquad (13)$$

different dienophiles: Q in the presence of $Mg(ClO_4)_2$ (1.6 M) and TCNE (Figure 7a). It should be emphasized that the slope of the linear correlation (−18) agrees with the value expected from eq 13 [$-(2.3RT)^{-1} = -17$ at 298 K]. Thus, the reactivity of anthracenes in the Diels−Alder reactions with both TCNE and Q in the presence of $Mg(ClO_4)_2$ is mainly determined by the ΔG_{et} values and is insensitive to the steric effects of alkyl group at the 9-position of anthracene. In the case of TCNE which is a strong electron acceptor, an electron-transfer process from anthracenes to TCNE occurs at a longer distance between the donor and acceptor prior to the bond formation, which requires a short distance as compared with the electron-transfer process. In the case of Q in the presence of $Mg(ClO_4)_2$, $Mg(ClO_4)_2$-promoted electron transfer also occurs prior to the bond formation, since the electron-transfer process is enhanced by the formation of complex formation of $Q^{\bullet -}$ with two $Mg(ClO_4)_2$ molecules.[22] On the other hand, no enhancement of the concerted process is attained by the presence of $Mg(ClO_4)_2$ which cannot form the complex with Q.

SCHEME 3



The k_{obs} values of the Diels−Alder reaction of anthracenes with the MVK−Sc(OTf)$_3$ complex are also linearly correlated with ΔG_{et} as shown in Figure 7b. However, the slope of the linear correlation (12) in Figure 7b is smaller than those expected from eq 13, and more importantly the log k_{obs} values are by far larger than those expected from the single linear correlation of log k_{obs} vs ΔG_{et} for the Diels−Alder reactions with TCNE and Q in Figure 7a. Such a significant difference from the linear correlation of the Diels−Alder reactions via electron transfer indicates that the Diels−Alder reactions of anthracenes with the MVK−Sc(OTf)$_3$ complex do not proceed via an electron-transfer pathway. The LUMO level of the MVK−Sc(OTf)$_3$ complex is significantly lowered as compared with that of MVK as indicated by the positive shift in the one-electron reduction potential (vide supra). The lower LUMO level of the MVK−Sc(OTf)$_3$ complex would result in the stronger orbital interaction with anthracenes, leading to the enhancement of the reactivity of the concerted process. Although an electron-transfer process is also enhanced by the complex formation of MVK with Sc(OTf)$_3$ as shown in Figure 5, the strong orbital interaction between anthracenes and the MVK−Sc(OTf)$_3$ complex results in a much faster rate than the corresponding electron transfer rate (Figure 7). The highly localized unpaired electron at the γ-carbon of MVK in the MVK$^{\bullet-}$−Sc(OTf)$_3$ complex as indicated by the ESR spectrum in Figure 6 indicates that the LUMO orbital coefficient is also highly localized at the γ-carbon of MVK in the MVK−Sc(OTf)$_3$ complex. In such a case, the bond formation process may be highly asynchronous, when the initial C−C bond formation may occur between the less sterically hindered carbon (10 position) of 9-methylanthracene and the γ-carbon of MVK in the MVK−Sc(OTf)$_3$ complex predominantly over the 9-position due to the steric hindrance of methyl group as shown in Scheme 3. This can account for the regioselective addition of MVK to 9-methylanthracene and also other 9-alkylanthracenes in Table 1.

Summary and Conclusions

Sc(OTf)$_3$ promotes both Diels−Alder reactions of anthracenes with the MVK−Sc(OTf)$_3$ complex and photoinduced electron transfer from various electron donors to the MVK−Sc(OTf)$_3$ complex. The saturated dependence of the second-order rate constant of Diels−Alder reaction and electron transfer with respect to concentration of Sc(OTf)$_3$ reveals that MVK−Sc(OTf)$_3$ complex reacts directly with anthracenes or electron donors. Extensive comparisons of Diels−Alder reactions of anthracenes with the MVK−Sc(OTf)$_3$ complex, TCNE, and Q in the presence of Mg(ClO$_4$)$_2$ reveal that Diels−Alder reactions of anthracenes with the MVK−Sc(OTf)$_3$ complex do not proceed via an electron transfer process. The bond formation process may be highly asynchronous, which induces regioselective addition of MVK to 9-alkylanthracene.

Acknowledgment. This work was partially supported by Grants-in-Aid (No. 16205020) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental section (S1), dependence of pseudo-first-order rate constant on [MVK] for Diels−Alder reaction of anthracenes with the MVK−Sc(OTf)$_3$ complex (S2), fluorescence decay profiles of electron donors in the absence and presence of Sc(OTf)$_3$ (S3), Stern−Volmer plots for fluorescence quenching by MVK and the MVK−Sc(OTf)$_3$ complex (S4), plots of $E_{ox} - (\Delta G^{\ddagger}/e)$ vs $(\Delta G^{\ddagger}/e)^{-1}$ in the absence and presence of Sc(OTf)$_3$ (S5). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Fringueli, F.; Taticchi, A. *The Diels−Alder Reaction. Selected Practical Methods*; John Wiley: New York, 2002. (b) *Cycloaddition Reactions in Organic Synthesis*; Kobayashi, S., Jrgensen, K. A., Eds.; Wiley-VCH: Weinheim, 2002.

(2) For recent reviews, see (a) Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1650. (b) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, *527*, 7. (c) Rechavi, D.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 3467. (d) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668.

(3) (a) Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000**, *33*, 325. (b) Evans, D. A.; Johnson, J. S. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Vol. 3, pp 1178−1235 and references therein.

(4) (a) Houk, K. N.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (b) Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81. (c) Dewar, M. J. S.; Jie, C. *Acc. Chem. Res.* **1992**, *25*, 537. (d) Horn, B. A.; Herek, J. L.; Zewail, A. H. *J. Am. Chem. Soc.* **1996**, *118*, 8755. (e) Sustmann, R.; Tappanchai, S.; Bandmann, H. *J. Am. Chem. Soc.* **1996**, *118*, 12555. (f) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(5) (a) Chen, J. S.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 12303. (b) McCarrick, M. A.; Wu, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1992**, *114*, 1449. (c) Jorgensen, W. L.; Lim, D.; Blake, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 2936. (d) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127. (e) Loncharich, R. J.; Brown, F. K.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 1129.

(6) (a) Domingo, L. R.; Aurell, M. J.; Pérez, P.; Contreras, R. *J. Org. Chem.* **2003**, *68*, 3884. (b) Singleton, D. A.; Schulmeier, B. E.; Hang, C.; Thomas, A. A.; Leung, S.-W.; Merrigan, S. R. *Tetrahedron* **2001**, *57*, 5149. (c) Froese, R. D. J.; Coxon, J. M.; West, S. C.; Morokuma, K. *J. Org. Chem.* **1997**, *62*, 6991.

(7) (a) Houk, K. N.; Wilsey, S. L.; Beno, B. R.; Kless, A.; Nendel, M.; Tian, J. *Pure Appl. Chem.* **1998**, *70*, 1947. (b) Beno, B. R.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4816.

(8) (a) Fukuzumi, S.; Kochi, J. K. *Tetrahedron* **1982**, *38*, 1035. (b) Fukuzumi, S.; Kochi, J. K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 969. (c) Dern, M.; Korth, H.-G.; Kopp, G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 337. (d) Sustmann, R.; Dern, M.; Kasten, R.; Sicking, W. *Chem. Ber.* **1987**, *120*, 1315. (e) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309.

(9) (a) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227. (b) Sustmann, R.; Lücking, K.; Kopp, G.; Rese, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1713. (c) Sustmann, R.; Korth, H.-G.; Nüchter, U.; Siangouri-Feulner, I.; Sicking, W. *Chem. Ber.* **1991**, *124*, 2811. (d) Yamago, S.; Ejiri, S.; Nakamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 5344.

(10) (a) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (b) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80. (c) Mattay, J.; Trampe, G.; Runsink, J. *Chem. Ber.* **1988**, *121*, 1991. (d) Lewis, F. D. *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C, p 1. (e) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1308. (f) Bauld, N. L. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1992; Vol. 2, p 1.

(11) (a) Takahashi, Y.; Kochi, J. K. *Chem. Ber.* **1988**, *121*, 253. (b) Kim, E.; Christl, M.; Kochi, J. K. *Chem. Ber.* **1990**, *123*, 1209. (c) Sun, D.; Hubig, S. M.; Kochi, J. K. *J. Photochem. Photobiol., A* **1999**, *122*, 87. (d) Fukuzumi, S.; Okamoto, T.; Ohkubo, K. *J. Phys. Chem. A* **2003**, *107*, 5412.

(12) (a) Mikami, K.; Matsumoto, S.; Okubo, Y.; Fujitsuka, M.; Ito, O.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2000**, *122*, 2236. (b) Vassilikogiannakis, G.; Orfanopoulos, M. *Tetrahedron Lett.* **1997**, *38*, 4323. (c) Mikami, K.; Matsumoto, S.; Tonoi, T.; Okubo, Y.; Suenobu, T.; Fukuzumi, S. *Tetrahedron Lett.* **1998**, *39*, 3733.

(13) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99.

(14) (a) Sprott, K. T.; Corey, E. J. *Org. Lett.* **2003**, *5*, 2465. (b) Corey, E. J.; Shibata, T.; Lee, T. W. *J. Am. Chem. Soc.* **2002**, *124*, 3808. (c) Ryu, D. H.; Lee, T. W.; Corey, E. J. *J. Am. Chem. Soc.* **2002**, *124*, 9992. (d) Faller, J. W.; Grimmond, B. J.; D'Alliessi, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 2525. (e) Ishihara, K.; Kurihara, H.; Matsumoto, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 6920. (f) Evans, D. A.; Miller, S. J.; Lectka, T.; von Matt, P. *J. Am. Chem. Soc.* **1999**, *121*, 7559. (g) Evans, D. A.; Wu, J. *J. Am. Chem. Soc.* **2003**, *125*, 10162. (h) Ryu, D. H.; Zhou, G.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 4800. (i) Davies, H. M. L.; Dai, X. *J. Am. Chem. Soc.* **2004**, *126*, 2692.

(15) (a) Paquette, L. A. In *Asymmetric Synthesis*; Morison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 456−478. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876. (c) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. (d) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070.

(16) (a) Otto, S.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1999**, *121*, 6798. (b) Otto, S.; Boccaletti, G.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1998**, *120*, 4238. (c) Otto, S.; Bertoncin, F.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1996**, *118*, 7702. (d) Pindur, U.; Lutz, G.; Otto, C. *Chem. Rev.* **1993**, *93*, 741. (e) Fringuelli, F.; Piermatti, O.; Pizzo, F.; Vaccaro, L. *Eur. J. Org. Chem.* **2001**, 439.

(17) (a) Doyle, M. P.; Phillips, I. M.; Hu, W. *J. Am. Chem. Soc.* **2001**, *123*, 5366. (b) Roush, W. R.; Barda, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 7402.

(18) (a) Kumar, A. *Chem. Rev.* **2001**, *101*, 1. (b) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007. (c) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29.

(19) Photochemical reactions have also been accelerated by complexation of chromophore with Lewis acids; see (a) Lewis, F. D.; Howard, D. K.; Oxman, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 3344. (b) Lewis, F. D.; Howard, D. K.; Oxman, J. D.; Upthagrove, A. L.; Quillen, S. L. *J. Am. Chem. Soc.* **1986**, *108*, 5964. (c) Lewis, F. D.; Quillen, S. L.; Hale, P. D.; Oxman, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1261. (d) Lewis, F. D.; Barancyk, S. V. *J. Am. Chem. Soc.* **1989**, *111*, 8653. (e) Lewis, F. D.; Barancyk, S. V.; Burch, E. L. *J. Am. Chem. Soc.* **1992**, *114*, 3866.

(20) (a) Fukuzumi, S. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 4, pp 3−67. (b) Fukuzumi, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1. (c) Fukuzumi, S. *Org. Biomol. Chem.* **2003**, *1*, 609. (d) Fukuzumi, S.; Ohkubo, K. *Chem.*−*Eur. J.* **2000**, *6*, 4532.

(21) For the metal ion-promoted photoinduced electron transfer, see (a) Fukuzumi, S.; Itoh, S. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., von Bünau, G., Eds.; Wiley: New York, 1998; Vol. 25, pp 107−172. (b) Fukuzumi, S.; Satoh, N.; Okamoto, T.; Yasui, K.; Suenobu, T.; Seko, Y.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **2001**, *123*, 7756. (c) Fukuzumi, S.; Mori, H.; Imahori, H.; Suenobu, T.; Araki, Y.; Ito, O.; Kadish, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 12458.

(22) (a) Fukuzumi, S.; Ohkubo, K.; Okamoto, T. *J. Am. Chem. Soc.* **2002**, *124*, 14147. (b) Fukuzumi, S.; Okamoto, T. *J. Am. Chem. Soc.* **1993**, *115*, 11600.

(23) Only one regioisomer is also obtained selectively in the Diels−Alder reaction of 9-methylanthracene with MVK in the presence of $\mathrm{Sc[B(C_6F_5)_4]_3}$.

(24) (a) Yuasa, J.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2002**, *124*, 12566. (b) Yuasa, J.; Suenobu, T.; Ohkubo, K.; Fukuzumi, S. *Chem. Commun.* **2003**, 1070.

(25) The k_{obs} value at high concentration of $\mathrm{Sc[B(C_6F_5)_4]_3}$ could not be determined because $\mathrm{Sc[B(C_6F_5)_4]_3}$ was not soluble in MeCN at high concentrations.

(26) In the presence of $\mathrm{Sc(OTf)_3}$ (5.0×10^{-1} M), 63% of MVK forms the complex with $\mathrm{Sc(OTf)_3}$.

(27) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(28) Fukuzumi, S.; Fujita, M.; Otera, J.; Fujita, Y. *J. Am. Chem. Soc.* **1992**, *114*, 10271.

(29) The work term (w_{p}) which is the energy required to bring the products to within the donor−acceptor complex is neglected in photoinduced electron-transfer reactions.[28]

(30) For the one-electron oxidation potential of $\mathrm{Ru(bpy)_3}^{2+*}$, see Kavarnos, G.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. For the one-electron oxidation potentials of $\mathrm{AcrH_2}$*, see Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

(31) The singlet excitation energies (eV) were obtained from the absorption and emission spectra: $\mathrm{AcrH_2}$, 3.90 eV; anthracene, 3.34 eV; 9-methylanthracene, 3.10 eV, 9,10-dimethylanthracene, 2.99 eV; 9,10-dibromoanthracene, 2.93 eV; and 9-cyanoanthracene, 2.94 eV.

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

(33) Such localization of the unpaired electron and negative charge has also been observed in the $\mathrm{Sc(OTf)_3}$ complex with pyrene radical anion; see Fukuzumi, S.; Yuasa, J.; Satoh, N.; Suenobu, T. *J. Am. Chem. Soc.* **2004**, *126*, 7585.

(34) Fukuzumi, S.; Nishizawa, N.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1985**, 371.

(35) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928.