Magnesium Perchlorate-Catalyzed Diels–Alder Reactions of Anthracenes with *p*-Benzoquinone Derivatives: Catalysis on the Electron Transfer Step

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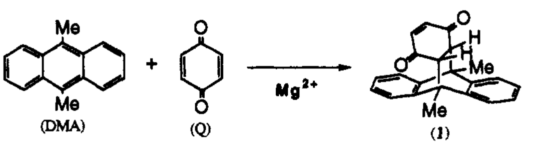
There has recently been increasing interest in the important role of electron-transfer processes as the activation step for some Diels–Alder reactions of electron-rich dienes having high-lying HOMOs with electron-deficient dienophiles having low-lying LUMOs.[1] The photochemical cycloadditions *via* photosensitized electron-transfer and charge-transfer irradiation of the electron donor–acceptor complexes formed between dienes and dienophiles have also been well documented.[2,3] However, the possible contribution of electron transfer in thermal Diels–Alder reactions has so far been limited to those with powerful dienophiles as strong electron acceptors.[1] This study reports that Diels–Alder reactions of anthracene with *p*-benzoquinone derivatives, which have been regarded as inert or weak dienophiles,[4] proceed efficiently in the presence of $Mg(ClO_4)_2$ in acetonitrile (MeCN) *via* Mg^{2+}-catalyzed electron transfer from anthracene to *p*-benzoquinone derivatives.[5] The direct spectroscopic detection of complexes formed between the corresponding semiquinone radical anions and Mg^{2+}, combined with the kinetic analysis of the catalytic effect of Mg^{2+}, provides a confirmative basis for delineating the catalytic mechanism of Mg^{2+}.

Although the reaction of 9,10-dimethylanthracene (DMA, 1.5×10^{-2} M) and *p*-benzoquinone (Q, 2.5×10^{-2} M) is sluggish in MeCN at 298 K, the addition of $Mg(ClO_4)_2$ (9.09×10^{-1} M) results in the efficient [4 + 2] cycloaddition to yield the adduct selectively (eq 1).[6] The [4 + 2] cycloaddition of anthracene and



(1)

9-methylanthracene with *p*-benzoquinone derivatives (X-Q; X = 2,5-Cl_2 and 2,5-Me_2) also occurs efficiently in the presence of $Mg(ClO_4)_2$ to yield the corresponding adducts. The rates of reactions of DMA with X-Q were determined by monitoring the disappearance of the absorbance due to DMA (λ_{max} = 398 nm, $\epsilon_{max} = 7.5 \times 10^3$ M^{-1} cm^{-1}). The rates obeyed second-order kinetics, showing a first-order dependence on each reactant concentration. The observed second-order rate constant (k_{obs}) increases with an increase in [Mg^{2+}] to exhibit first-order dependence on [Mg^{2+}] at low concentrations, changing to second-order dependence at high concentrations, as shown in Figure 1a.[7]

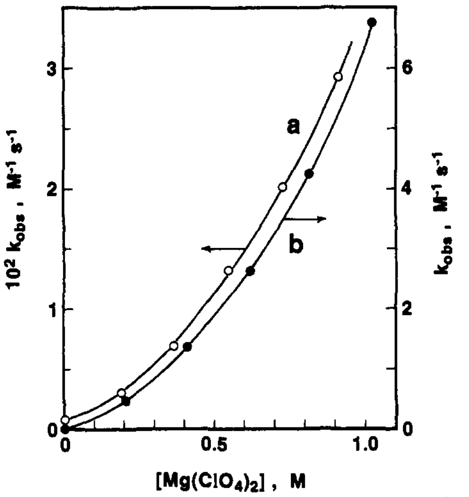


Figure 1. Dependence of k_{obs} on [$Mg(ClO_4)_2$] for (a) Diels–Alder reaction of DMA (1.3×10^{-3} M) with Q (3.6×10^{-1} M) and (b) electron transfer from CoTPP (1.0×10^{-5} M) to Q (3.7×10^{-3} M) in the presence of $Mg(ClO_4)_2$ in deaerated MeCN at 298 K.

No electron transfer from CoTPP (TPP = tetraphenylporphyrin dianion) to Q has occurred in MeCN at 298 K. In the presence of $Mg(ClO_4)_2$, however, efficient electron transfer from CoTPP to Q occurs to yield $CoTPP^+$. The electron-transfer rates obeyed second-order kinetics, showing a first-order dependence on each reactant concentration. There is a striking similarity with respect to the dependence of k_{obs} on [Mg^{2+}] between the electron-transfer reaction (Figure 1b) and the Diels–Alder reaction (Figure 1a), despite of the large difference in their reactivities.

When CoTPP is replaced by a stronger one-electron reductant (decamethylferrocene, [$Fe(C_5Me_5)_2$]), electron transfer from $Fe(C_5Me_5)_2$ to Q in the presence of $Mg(ClO_4)_2$ is complete upon mixing. The transient spectra of semiquinone radical anion in the presence of different concentrations of $Mg(ClO_4)_2$ are obtained by measuring the change in initial absorbance at various wavelengths with use of a stopped-flow spectrophotometer.[8] The absorption spectrum of Q^- in the presence of 1.0×10^{-2} M Mg^{2+} (λ_{max} = 590 nm) is significantly red-shifted as compared to that in the absence of Mg^{2+} (λ_{max} = 422 nm). Further addition of Mg^{2+} results in a blue shift to λ_{max} = 415 nm with a clean isosbestic point. Such spectroscopic changes may be interpreted as being due to the formation of complexes between Q^- and Mg^{2+}, which

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[5] Lithium perchlorate in diethyl ether has recently been reported to accelerate Diels–Alder reactions. The role of Li^+ has been discussed extensively: (a) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595. (b) Waldmann, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1306. (c) Smith, D. A.; Houk, K. N. *Tetrahedron Lett.* **1991**, *32*, 1549. (d) Forman, M. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 2761. (e) Desimoni, G.; Faita, G.; Righetti, P. P.; Tacconi, G. *Tetrahedron* **1991**, *47*, 8399. (f) Pagni, R. M.; Kabalka, G. W.; Bains, S.; Plesco, M.; Wilson, J.; Bartmess, J. *J. Org. Chem.* **1993**, *58*, 3130.

[6] The yield of **1** was 100%. Anal. Calcd for $C_{22}H_{18}O_2$ (**1**): C, 84.05; H, 5.77. Found: C, 83.73; H, 5.62. The ^1H NMR measurements were performed using a JNM-GSX-400 NMR spectrometer. ^1H NMR of **1** (CD_3CN): δ 2.24 (s, 6H), 3.45 (s, 2H), 7.3–7.7 (m, 8H).

[7] In contrast, the linear dependence of k_{obs} on [Li^+] has been reported for the Diels–Alder reaction between DMA and acrylonitrile in $LiClO_4$–diethyl ether solution, in which Li^+ is claimed to act as the Lewis acid by complexing with the cyano group nitrogen of acrylonitrile.[5d] However, a similar second-order dependence of k_{obs} on [Li^+] has been reported for the reactions of DMA with fumaronitrile and dimethyl acetylenedicarboxylate.[5d]

[8] For the absorption spectrum of Q^- in the absence of Mg^{2+} in MeCN, see: Fukuzumi, S.; Yorisue, T. *J. Am. Chem. Soc.* **1991**, *113*, 7764.

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Table I. Absorption Maxima (λ_{max}) of Semiquinone Radical Anion ($X\text{–}Q^{\bullet-}$), $X\text{–}Q^{\bullet-}\text{–}Mg^{2+}$, and $X\text{–}Q^{\bullet-}\text{–}2Mg^{2+}$ Complexes Formed in the Electron-Transfer Reduction of X–Q in the Presence of $Mg(ClO_4)_2$ and Formation Constants of $X\text{–}Q^{\bullet-}\text{–}2Mg^{2+}$ (K_2) in the Electron-Transfer Reduction of X–Q and the Diels–Alder Reactions of DMA with X–Q in MeCN at 298 K

	λ_{max}, nm				
p-benzoquinone form	$X\text{–}Q^{\bullet-}$	$X\text{–}Q^{\bullet-}\text{–}Mg^{2+}$	$X\text{–}Q^{\bullet-}\text{–}2Mg^{2+}$	K_2,[a] M^{-1}	K_2,[b] M^{-1}
p-benzoquinone	422	590	410	4.5	3.9 (4.1)[c]
2,5-dichloro-*p*-benzoquinone	425	645	440	2.1	2.7
2,5-dimethyl-*p*-benzoquinone	436	615	425	4.8	4.6

[a] Determined from the spectral change in the presence of Mg^{2+}. [b] Determined from the dependence of k_{obs} on $[Mg^{2+}]$ based on eq 3. The experimental errors are ±10%. [c] The value in parentheses is obtained from electron transfer from CoTPP to Q in the presence of Mg^{2+} in MeCN at 298 K. The experimental error is ±10%.

requires two steps.[9] The first step is the formation of a 1:1 complex ($Q^{-}\text{–}Mg^{2+}$), and the second step is an additional addition of Mg^{2+} to form a 1:2 complex ($Q^{-}\text{–}2Mg^{2+}$). The formation of such complexes is also confirmed by the ESR spectra observed in the electron-transfer reaction from $Fe(C_5Me_5)_2$ to Q in the presence of Mg^{2+} in deaerated MeCN by applying a rapid-mixing ESR technique.[10] From the spectral change at different Mg^{2+} concentrations is determined the formation constant (K_2) of the 1:2 complex, although the formation constant (K_1) of the 1:1 complex is too large to be determined accurately. Similar spectral changes with respect to $[Mg^{2+}]$ are observed for $X\text{-}Q^{-}$. The K_2 values and the λ_{max} values of 1:1 and 1:2 complexes of $X\text{-}Q^{-}$ and Mg^{2+} are listed in Table I.

The complex formation of Q^{-} and Mg^{2+} should result in the positive shift of the one-electron reduction potential of Q (E_{red}), and the Nernst equation may be given by eq 2, where E^0_{red} is the

$$E_{red} = E^0_{red} + (2.3RT/F)\log K_1[Mg^{2+}](1 + K_2[Mg^{2+}]) \quad (2)$$

one-electron reduction potential of Q in the absence of Mg^{2+}, and $K_1[Mg^{2+}] \gg 1$.[11] From eq 2 is derived the dependence of the observed rate constant of electron transfer (k_{obs}) on $[Mg^{2+}]$, as given by eq 3, where k_0 is the rate constant in the absence of Mg^{2+}. The validity of eq 3 is confirmed by the linear plot of $(k_{obs}$

$$(k_{obs} - k_0)/[Mg^{2+}] = k_0K_1(1 + K_2[Mg^{2+}]) \quad (3)$$

$- k_0)/[Mg^{2+}]$ vs $[Mg^{2+}]$ for the data in Figure 1b. Thus, from the slope and intercept is obtained the K_2 value (4.1 M^{-1}), which agrees well with that (4.5 M^{-1}) determined independently from the direct spectral change of Q^{-} in the presence of Mg^{2+}. On the other hand, the same plot (eq 3) for the Mg^{2+}-catalyzed Diels–Alder reaction of DMA with Q (Figure 1a) also gives a straight line. The K_2 values obtained from the linear plots for the Diels–Alder reactions of DMA with X-Q in MeCN at 298 K are also listed in Table I, where the K_2 value decreases with a decrease in the electron-donating ability of $X\text{-}Q^{-}$ (X = 2,5-Me_2 > H > 2,5-Cl_2), agreeing well with those obtained directly from the spectral change of $X\text{-}Q^{-}$ in the presence of Mg^{2+}. Such agreements for each quinone strongly suggest that the catalysis of Mg^{2+} in the Diels–Alder reactions of DMA with X-Q is essentially the same as that in the electron-transfer reduction of X-Q. Thus, the Mg^{2+}-catalyzed electron transfer from anthracenes to X-Q may be a rate-determining step of the Diels–Alder reactions. In such a case, the K_2 values should be the same, irrespective of anthracene derivatives, since the formation of the 1:2 complex of Q^{-} and Mg^{2+} is independent of anthracene derivatives. In fact, the K_2 values derived from the Diels–Alder reactions of DMA, 9-methylanthracene, and anthracene with Q in MeCN at 333 K are the same ($K_2 = 2.1 \pm 0.3$ M^{-1}), despite the significant difference in their reactivities: $k_0K_1 = 3.5 \times 10^{-2}$, 6.2×10^{-3}, and 1.4×10^{-4} M^{-2} s^{-1}, respectively. Moreover, it has been confirmed that no 1:2 complex is formed between Q and Mg^{2+}.[12] Only the one-electron reduced species, *i.e.*, $X\text{-}Q^{-}$, can form the 1:2 complex with Mg^{2+}. Thus, the role of Mg^{2+} to activate the weak dienophiles (X-Q) is ascribed to the 1:1 and 1:2 complex formation of $X\text{-}Q^{-}$ and Mg^{2+}, which results in an increase in the rate of electron transfer from anthracenes as well as one-electron reductants to X-Q with an increase in $[Mg^{2+}]$, exhibiting first-order and second-order dependence on $[Mg^{2+}]$, respectively.

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[9] For an excellent review on anion radicals and their transition-metal complexes, see: Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.

[10] The *g* value of the $Q^{-}\text{–}2Mg^{2+}$ complex is 2.0043, which is smaller than the *g* value of Q^{-} (2.0049) because of the decrease in the spin density on the oxygen atom in the Mg^{2+} complex.

[11] A similar potential shift has been observed for E_{red} in the presence of $HClO_4$ in MeCN: Fukuzumi, S.; Ishikawa, K.; Hironaka, K.; Tanaka, T. *J. Chem. Soc., Perkin Trans. 2* **1987**, 751.

[12] The ^{13}C NMR signals of the carbonyl carbon of Q in CD_3CN is little affected by the addition of $Mg(ClO_4)_2$, exhibiting only slight upfield shifts which were proportional to $[Mg^{2+}]$.