Effects of magnesium salts on photoinduced electron transfer reaction between ammonia, 2,5-dimethylhexa-2,4-diene, and 9-cyanophenanthrene

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A R T I C L E   I N F O

A B S T R A C T

Mechanistic studies and product analyses were performed on the single electron transfer (SET) promoted photoamination reaction between 2,5-dimethylhexa-2,4-diene (**1**) and 9-cyanophenanthrene in order to gain a comprehensive understanding of the effects of additive metal salts. The product selectivity of this process was found to be dramatically increased by the addition of Mg^{2+} salts. An investigation involving the analyses of fluorescence and time-resolved absorption spectroscopic properties reveals that Mg^{2+} enhances the rate of the initial SET step and stabilizes the resulting radical ion pair in this photoreaction.

1. Introduction

Photochemical reactions proceed by way of high-energy intermediates, such as electronically excited states, radical ions, and radicals. The highly reactive nature of these species enables some photochemical reactions to occur through thermally forbidden pathways that lead to the construction of highly strained structures. However, these processes are often attended by competitive and secondary reactions, which result in reactant degradation and formation of complex product mixtures.

Much effort has been given to finding ways to improve photoreaction selectivities, especially in the case of electron transfer photochemical reactions. One approach involves the use of additives. An example of this is found in the dramatic improvement seen in the efficiencies and the selectivities of photoinduced electron transfer (PET) reactions brought about by the addition of aromatic hydrocarbons (e.g., phenanthrene and biphenyl) that serve as redox photosensitizers.[1] Specific inorganic metal salts, such as $Mg(ClO_4)_2$, act as enhancers of charge separation[2] and lead to the improvement of yields and selectivities of various

photoreactions.[3] The salts have advantages over organic additives in terms of synthetic applications since they can be easily removed after termination of photoirradiation by using simple extraction techniques. Thus far, charge separation effects of salts have only been investigated by using either spectroscopic approaches or product distribution analyses independently. Studies, in which both mechanistic explorations and product analyses are carried out simultaneously within a single photoreaction system in order to gain a comprehensive understanding of the salt effects, are rare.[4]

Previously, we reported that the photoamination reaction, promoted by irradiation of a acetonitrile–water solution of ammonia, 2,5-dimethylhexa-2,4-diene (**1**), and 9-cyanophenanthrene (9-CP), leads to formation of the ammonia-incorporated dimer **2**[5] and the three-component adduct **3**[6] (Eq. 1).[7] It was proposed that this reaction is initiated by single electron transfer (SET) from **1** to excited singlet state of 9-CP (^{1}9-CP*),[8] giving **1**$^{•+}$, which reacts with ammonia to form the allylic radical intermediate **4**$^{•}$ (Scheme 1). Diffusion (out-of-cage) and coupling of **4** affords **2**, while radical coupling between **4**$^{•}$ and **5**$^{•}$ (protonated 9-CP$^{•-}$) within the solvent cage (in-cage) results in production of **3**.

$$(1)$$
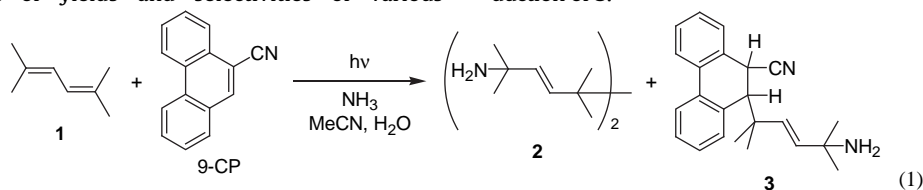
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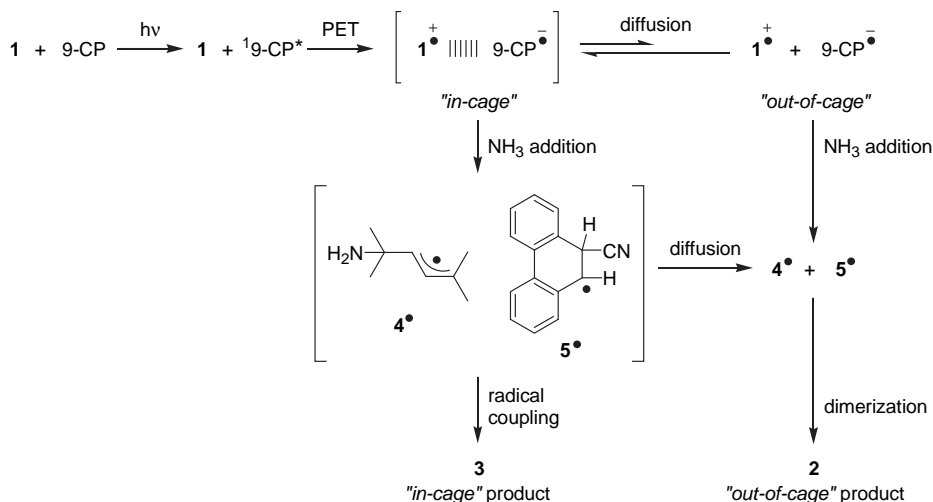
Scheme 1. Proposed mechanism for the formation of **2** and **3**.

Below, the results of a detailed examination of the effects of additives on the photoamination reaction of **1** are described. In particular, the effects of magnesium salts on the **2:3** product ratio, the fluorescence properties of 9-CP, and transients generated by using nanosecond laser flash photolysis (LFP) were evaluated.

2. Results and discussion

2.1. Improvement of product selectivity in the photoamination reaction of 1 caused by Mg²⁺

Photoirradiation of an acetonitrile–water (4:1, v/v) solution containing diene **1**, 9-CP and ammonia results in the formation of **2** and **3** in a **2:3** M ratio of 18:1 (Fig. 1).[7] A significant increase in product selectivity (**2:3**=81:1), that is, caused by the suppression of the formation of **3** occurs when Mg(ClO₄)₂ is present in the reaction mixture. In contrast, other metal perchlorates (LiClO₄, NaClO₄, KClO₄, Zn(ClO₄)₂, and AgClO₄), do not bring about any notable effects on the **2:3** ratio (16–24:1). Enhancement of the selectivity of the process also takes place when MgCl₂ and MgSO₄ (**2:3**=118:1 and 66:1, respectively) are present. In the case where biphenyl is employed as a redox photosensitizer,[1] a low selectivity of **2:3**=10:1 is obtained.
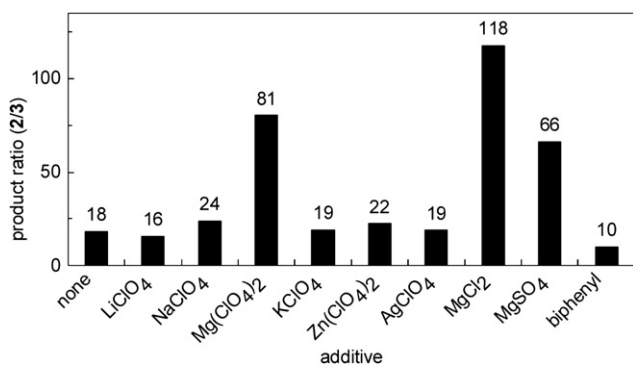

Figure 1. Effects of additives on photoamination of **1** with NH₃. Conditions: 300-W high-pressure mercury lamp, Pyrex filter, **1** (75 μmol), 9-CP (25 μmol), NH₃ (2.5 mmol), additive (2.5 μmol), in MeCN (4 mL)–H₂O (1 mL), under Ar, rt, 20 h. Product ratios were determined by ¹H NMR analyses.

The results summarized above indicate that no cation other than Mg²⁺ causes an enhancement in the **2:3** product selectivity and that the nature of the counter anion is also relevant. In the mechanistic pathway for this process (vide supra),[7] coupling between the respective radical cation- and radical anion-derived intermediates **4·** and **5·** takes place within the solvent cage to produce the 'in-cage' product **3**. Based on the observations made, it appears plausible that magnesium salts interfere with the radical coupling process by promoting separation of **1·⁺** and 9-CP·⁻ (Eq. 2).[2] The reason why only Mg²⁺ showed the drastic effects is yet unknown, but we suppose that higher charge density of the dicationic species might be responsible for the specific salt effects.

$$\left[\mathbf{1}^{+}_{\bullet} \; \text{||||||} \; \text{9-CP}^{-}_{\bullet} \right] \xrightarrow{\text{MgX}_2} \left[\mathbf{1}^{+}_{\bullet} \; \text{||||||} \; X^{-} \right] + \left[\text{Mg}^{2+} \; \text{||||||} \; \text{9-CP}^{-}_{\bullet} \right] \quad (2)$$

2.2. Exciplex quenching promoted by Mg(ClO₄)₂

For the purpose of gaining insight into the mechanistic features associated with the effects of magnesium salts, spectroscopic investigations were conducted. Fluorescence spectra of 9-CP in acetonitrile were measured in the absence and presence of Mg(ClO₄)₂ and/or **1**. In the absence of the additives, an acetonirile solution of 9-CP solution contains a fluorescence band with λ_{max} at 361 and 377 nm (Fig. 2a, solid line). No change in this spectrum was observed to occur when Mg(ClO₄)₂ was added, indicating that Mg²⁺ does not alter the fluorescence properties of 9-CP (Fig. 2b, dashed line).[9]
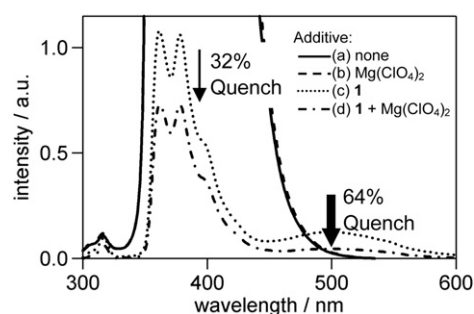

Figure 2. Effects of additives on the fluorescence of 9-CP (1.01×10^{-4} M) in MeCN (λ_{ex}=311 nm). Additive (0.10 M each): (a) none (solid line), (b) Mg(ClO₄)₂ (dashed line), (c) **1** (dotted line), (d) Mg(ClO₄)₂ and **1** (chain line).

The fluorescence of 9-CP is quenched by diene **1** at a near diffusion controlled rate (k_q=6.1×10⁹ M⁻¹ s⁻¹, from a Stern–Volmer analysis[10,11]) and a weak and broad emission (λ_{max} ~496 nm) with an isoemissive point of ~480 nm appears simultaneously (Fig. 2c,

dotted line). The quenching is associated with the formation of an singlet exciplex ($^1[1^{\delta+} \cdots 9\text{-CP}^{\delta-}]*$), which decays via three pathways including emission at 496 nm, nonradiative deactivation, and single electron transfer to form a radical ion pair ([$1^{\cdot+} \cdots 9\text{-CP}^{\cdot-}$]).

Both the monomer and exciplex emission of a mixture of **1** and 9-CP is diminished by the addition of Mg(ClO$_4$)$_2$ (Fig. 2d, chain line).[12] The exciplex emission is more effectively quenched (64% quenching) than the monomer emission (32% quenching). Thus, it appears that Mg^{2+} selectively interacts with the exciplex bringing about its decay by enhancing SET. The simultaneous decrease of monomer emission could be due to a shift in the equilibrium from the excited monomer to the exciplex as a result of exciplex consumption.[13]

2.3. Long-lived transient radical ion formation in the presence of Mg(ClO$_4$)$_2$

The results of LFP experiments show that irradiation of an acetonitrile solution of **1** and 9-CP results in the formation of transients with absorption maxima at 363 (k_{decay}=8.5×10^5 s^{-1}) and 425 (2.2×10^5 s^{-1}) nm (Fig. 3a). A substantial decrease in the rate constant for decay of the former species (k_{decay}=1.4×10^5 s^{-1}) occurs when Mg(ClO$_4$)$_2$ is present in the solution (Fig. 3b).[4,14] On the other hand, decay of the 425-nm band is only slightly changed (k_{decay}=1.7×10^5 s^{-1}) on addition of this salt. Thus, Mg^{2+} stabilizes the transient species with the 363-nm absorption maximum, but not the one associated with the 425-nm maximum.
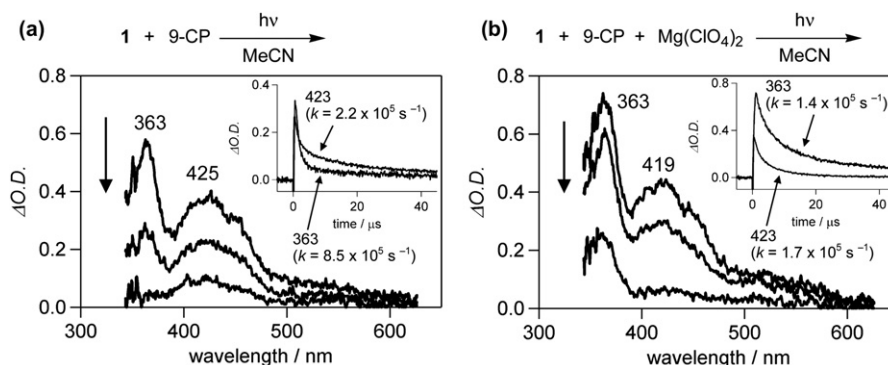
Support for the assignments of these transients was gained by using TD-DFT (time-dependent density functional theory) calculations (TD-UB3LYP/6-31+G*).[17] The results of the calculations reveal that electronic transitions should exist at 309 (f=0.74) and 422 (0.01) nm for the optimized structure of $1^{\cdot+}$, which exists in a *s-trans* conformation (dihedral angle around the central C–C single bond: 179°) (Fig. 5a and Chart 1). The calculated absorptions are at far shorter than the 362 and 471 nm transients observed in the LFP studies. A possible explanation for the differences between the experimentally observed and calculated spectra is that $1^{\cdot+}$ possesses a *s-cis*-like conformation in the reaction system, which should have a longer wavelength maxima than *s-trans*-$1^{\cdot+}$ owing to through-space electronic coupling.[15d] The transitions for *s-cis*-$1^{\cdot+}$ (dihedral angle: 32°) were calculated to take place at 336 (f=0.37) and 478 (0.03) nm (Fig. 5b and Chart 1). The results of a calculation on 9-CP$^{\cdot-}$ reveal that its major electronic transition should correspond to an absorption band at 406 nm (f=0.16), which well supports the assignment made to the 425-nm transient (Fig. 5c).

Based on these results, it can be concluded that the lifetime of $1^{\cdot+}$ is enhanced by the presence of Mg^{2+}, which suppresses back electron transfer (BET) from 9-CP$^{\cdot-}$ to $1^{\cdot+}$. The complex [Mg^{2+} ⋯ 9-CP$^{\cdot-}$] formed by the interaction of 9-CP$^{\cdot-}$ with Mg^{2+} possesses a positive charge and, consequently, it should repel $1^{\cdot+}$ slowing BET. The reason why only a slight effect was observed for Mg^{2+} on 9-CP$^{\cdot-}$ is uncertain at this point but it may be a result of the fact that the complex [Mg^{2+} ⋯ 9-CP$^{\cdot-}$] has different absorption properties

Figure 3. Time-resolved UV–vis absorption spectra of degassed MeCN solutions containing **1** (20 mM) and 9-CP (2 mM) in the (a) absence and (b) presence (0.1 M) of Mg(ClO$_4$)$_2$ at 0.1, 1.0, and 10.0 μs after LFP (λ_{ex}=355 nm). The insets are time profiles at 363 and 423 nm.

The transient in Figure 3 absorbing at 425 nm might be 9-CP$^{\cdot-}$. The 363-nm transient (Fig. 3) is assigned to $1^{\cdot+}$ by using a control LFP experiment with *N*-methylquinolinium tetrafluoroborate (NMQ$^+$BF$_4^-$) as an electron-accepting photosensitizer.[15] Pulsed irradiation of NMQ$^+$BF$_4^-$ in a solution containing **1** and toluene as a cosensitizer brings about formation of an intense transient absorption band with a maximum of 362 (lit. 365)[16] nm along with a weak and broad transient around 471 (lit. 470)[16] nm (Fig. 4).
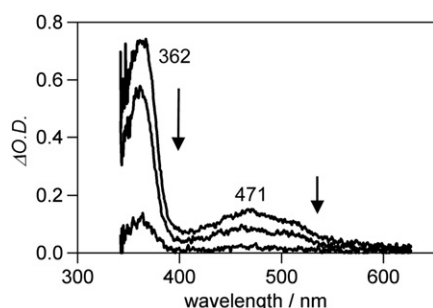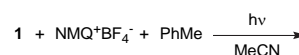

Figure 4. Time-resolved UV–vis absorption spectra of an aerated MeCN solution at 0.1, 1.0, and 10.0 μs after LFP (λ_{ex}=355 nm). **1** (20 mM), NMQ$^+$BF$_4^-$ (10 mM), toluene (1 M).

$$\text{1} + \text{NMQ}^+\text{BF}_4^- + \text{PhMe} \xrightarrow[\text{MeCN}]{h\nu}$$

than free 9-CP$^{\cdot-}$ or that Mg^{2+} influences other consumption pathways for 9-CP$^{\cdot-}$, such as protonation to form **5**$^{\cdot}$.[7]

3. Conclusion

In this investigation, we have successfully combined spectroscopic observations and product analysis in developing a comprehensive explanation for the effects of Mg^{2+} on the photoamination reaction of diene **1**. A dramatic improvement of the **2:3** product selectivity in this process was achieved by the addition of Mg^{2+} salts. Precise analyses of steady-state fluorescence and time-resolved absorption data show that the addition of Mg^{2+} causes an enhanced rate of decay of the exciplex $^1[1^{\delta+} \cdots 9\text{-CP}^{\delta-}]*$, and stabilization of the transient $1^{\cdot+}$. A plausible explanation for these effects is that Mg^{2+} enhances SET within the exciplex $^1[1^{\delta+} \cdots 9\text{-CP}^{\delta-}]*$ and promotes charge separation of the resulting radical ion pair [$1^{\cdot+} \cdots 9\text{-CP}^{\cdot-}$] by interacting with 9-CP$^{\cdot-}$. These phenomena lead to increased product selectivity by increasing the amount of the out-of-cage product **2** formed in the reaction.
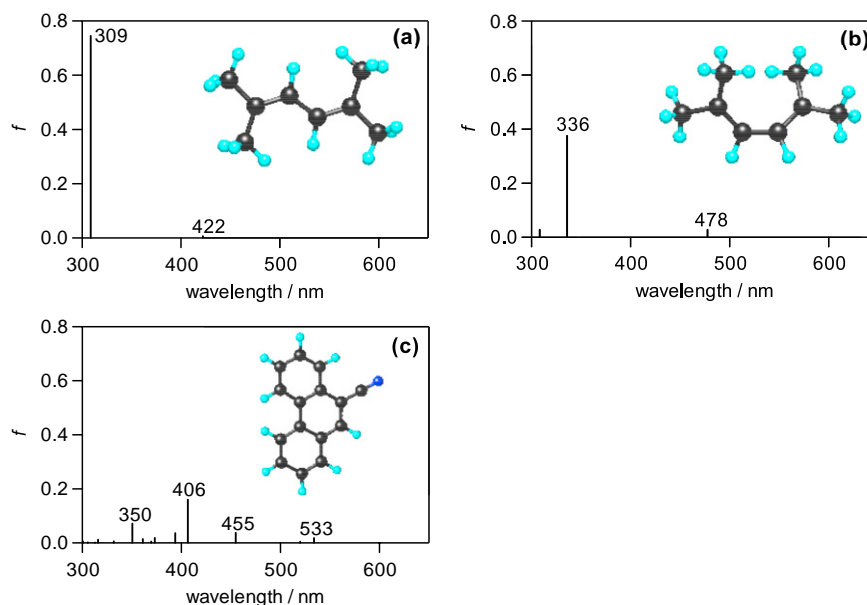
Figure 5. Electronic transition calculated with TD-DFT calculations (TD-UB3LYP/6-31+G*) of (a) *s-trans*-**1**·⁺, (b) *s-cis*-**1**·⁺, and (c) 9-CP·⁻.
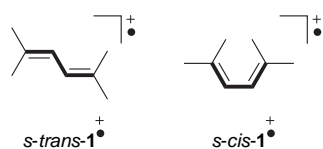

Chart 1. Two possible conformations of **1**·⁺.

This study represents one of only a few, in which both spectroscopic and product analyses are used to probe a single photoreaction system. In addition, the effort has provided a rare example where all of the common steps of a single PET reaction, including excited monomer, exciplex, solvent caged and free radical ion formation, are observed in either a direct or indirect manner.

4. Experimental section

4.1. Procedure used for the photoreaction

To a Pyrex glass tube (1 cmφ) was added an acetonitrile (4 mL)–water (1 mL) solution containing **1** (8.3 mg, 75 μmol), 9-CP (5.1 mg, 25 μmol), ammonia (43 mg, 2.5 mmol), and an additive (metal salt or biphenyl, 25 μmol). The solution was purged with argon for 5 min and then the tube was sealed with a rubber septum. After irradiation for 20 h by using a 300-W high-pressure mercury lamp, the photolysate was extracted with toluene–diethyl ether. The organic extracts were combined and concentrated in vacuo giving a crude mixture, on which ¹H NMR analysis was performed using tetrahydrofuran as an internal standard to determine the yields of **2** and **3** (34% and 3% based on the amount of **1** and 9-CP used, respectively, when additive was not used). Purification by silica gel chromatography (ethyl acetate after toluene) followed by HPLC (GPC column, chloroform) gave **2** as brown oil.

4.1.1. trans,trans-2,5,5,6,6,9-Hexamethyldeca-3,7-diene-2,9-diamine (2)[7]. ¹H NMR (300 MHz, CDCl₃) δ=0.94 (s, 12H, -Me), 1.20 (s, 12H, -Me), 1.6 (br s, 4H, –NH₂), 5.42 (d, J=16.1 Hz, 2H, olefin), 5.58 (d, J=16.1 Hz, 2H, olefin) ppm; ¹³C NMR (75 MHz, CDCl₃) δ=23.5 (4C, –Me), 31.4 (4C, -Me), 40.4 (2C, 4), 50.9 (2C, 4), 133.2 (2C, olefin), 137.4 (2C, olefin) ppm; MS (EI⁺) m/z=126 (100, M⁺/2), 110 (67, M⁺/

2–NH₂), 109 (56, M⁺/2–NH₃), 96 (26), 95 (19, M⁺/2–MeNH₂); IR (NaCl) ν=982, 1590 (H–N–H), 2965, 3285 (N–H), 3355 (N–H) cm⁻¹.

4.1.2. 10-(trans-4-Amino-1,1,4-trimethylpent-2-enyl)-9-cyano-9,10-dihydrophenanthrene (3)[7]. MS (EI⁺) m/z=315 (3, M⁺–Me), 204 (27, M⁺–CMe₂CH=CHCMe₂NH₂), 203 (27, 9-CP·⁺), 177 (22), 126 (100, H₂NCMe₂CH=CHCMe₂⁺), 110 (24, (Me₂C=CH–)₂⁺), 109 (54).

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