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### The Remarkable Effect of the Manganese Ion with Dioxygen on the Stability of $\pi$ -Conjugated Radical Cations

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Abstract: In this paper, nanosecond laser flash photolysis has been used to investigate the influence of metal ions on the kinetics of radical cations of a range of carotenoids (astaxanthin (ASTA), canthaxanthin (CAN), and  $\beta$ -carotene ( $\beta$ -CAR)) and various electron donors (1,4-diphenyl-1,3-butadiene (14DPB), 1,6-diphenyl-1,3,5-hexatriene (16DPH), 4-methoxy-trans-stilbene (4MeOSt), and trans-stilbene (trans-St)) in benzonitrile. Radical cations have been generated by means of photosensitized electron-transfer (ET) using 1,4-dicyanonaphthalene (14DCN) and biphenyl (BP). The kinetic decay of CAR'+ shows a strong dependence on the identity of the examined metal ion. For example, whereas NaClO<sub>4</sub> has a weak effect on the kinetics of  $CAR^{+}$ , Ni(ClO<sub>4</sub>)<sub>2</sub> causes a strong retardation of the decay of CAR<sup>++</sup>. It is also interesting to note that Mn<sup>2+</sup>, which is a biologically relevant metal ion, shows the strongest effect of all the investigated metal ions (e.g., in the presence of Mn2+ ions, the half-life  $(t_{1/2})$  of CAN<sup>++</sup>  $(t_{1/2} > 90 \text{ ms})$  is more than three orders of magnitude higher than in the absence of the metal ions  $(t_{1/2} \approx 16 \,\mu s))$ . Furthermore, the influence of metal-ion and oxygen concentrations on the kinetics of CAR'+ reveals their pronounced effect on the kinetic decay of CAR++. However, these

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remarkable effects are greatly diminished if either oxygen or metal ions are removed from the investigated solutions. Therefore, it can be concluded that oxygen and metal ions interact cooperatively to induce the observed substantial effects on the stabilities of CAR<sup>+</sup>. These results are the first direct observation of the major role of oxygen in the stabilization of radical cations, and they support the earlier mechanism proposed by Astruc et al. for the role of oxygen in the inhibition of cage reactions. On the basis of these results, the factors that affect the stability of radical cations are discussed and the mechanism that shows the role of oxygen and metal ions in the enhancement of radical-cation stability is described.

#### Introduction

A special salt effect was first observed by Winstein et al. during their study of the salt effect on the solvolysis reactions of alkyl arylsulfonates. They observed a sharp rise in the rate constant at low salt concentrations, which cannot be explained by normal salt effects. However, at higher salt concentrations, an increase in the rate constant follows the normal salt effect, which depends on the ionic strength.<sup>[1]</sup>

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Winstein et al. attributed the initial sharp rise in the rate constant, which he called a special salt effect, to the prevention of the return of the solvent-separated ion pair (SSIP) to contact ion pair (CIP) (Scheme 1).<sup>[1]</sup>





For photoinduced electron transfer (PET) reactions, there are many examples of the remarkable effects of various salts on these reactions and the dependence of their efficiencies on the nature of the metal ion used.<sup>[2-8]</sup> For example, Moore et al. studied the influence of salts on the intramolecular charge-separated state (CAR'+-P-Q'-) of a carotenoporphyrin-quinone triad (i.e., tetraarylporphyrin (P) covalently linked to both a carotenoid (CAR) and a quinone (Q)) induced by visible-light excitation of the porphyrin moiety in the triad (Scheme 2). They found that saturation of a solution of the triad with tetra-n-butylammonium tetrafluoroborate in chloroform significantly enhanced the yield and the half-life of carotenoid radical cations.<sup>[9]</sup> Also, Mizuno et al. investigated extensively the role of metal salts on photoiso-

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Scheme 2. Different pathways obtained following excitation of the porphyrin moiety (p) in the carotenoporphyrin–quinone triad (CAR-P-Q). BET: back electron transfer.

merization, photoxygenation, and  $TiO_2$ -catalyzed reactions, and they found that metal salts have significant effects on the quantum yields of various products.<sup>[4–7]</sup>

The significant effects produced by the salts in photoinduced electron-transfer reactions can be interpreted as described in Scheme 3. Following the PET reaction, the initial-



Scheme 3. Influence of salt  $[M^+, X^-]$  on the contact ion pair (CIP)  $[A^{++}\!\!,B^{+-}].$ 

ly formed CIP  $[A^{++},B^{--}]$  undergoes a fast, almost diffusioncontrolled double ion-exchange reaction with the salt  $[M^+,X^-]$  to form  $[A^{++},X^-]$  and  $[M^+,B^{--}]$ , which results in the suppression of the back-electron-transfer (BET) reaction between the radical ions of the initially formed CIP (Scheme 3).<sup>[2,4-7]</sup>

Of particular interest is the role of oxygen in the special salt effect.<sup>[2–6,10–12]</sup> In a series of elegant studies by Astruc's group,<sup>[2,10–12]</sup> they investigated the influence of salts on the reduction of  $O_2$  by iron(I) complexes (D), and they found that in the presence of sodium hexafluorophosphate,  $D^+PF_6^-$  and Na<sub>2</sub>O<sub>2</sub> were formed, whereas the formation of cage products, which are formed in the absence of salt, was totally inhibited (Scheme 4). These observations were attributed to the shift in the equilibrium of the ion-exchange reaction toward the formation of  $[D^{++}, PF_6^-]$  and  $[Na^+, O_2^{--}]$  due to the metal-induced dismutation of superoxide to perox-



Scheme 4. Influence of NaPF<sub>6</sub> on the CIP  $[D^{+},O_2^{+-}]$  formed following the reduction of O<sub>2</sub> by iron (I) complexes (D).

ide.<sup>[2,10-13]</sup> Furthermore, a similar mechanism was also used to explain the influence of salts in the presence of oxygen on the photooxidation of tertiary methylamines when using 9,10-dicyanoanthracene as sensitizer.<sup>[2,3]</sup> Therefore, according to these results, oxygen was proposed to have a significant role through the formation of superoxide anion.

In PET reactions in the presence of oxygen, superoxide anion  $(O_2^{-})$  can be formed if the ET reaction from the initially formed radical anion to oxygen is thermodynamically

$$D + X \xrightarrow{h\nu} [D^{+}, X^{-}]$$

$$O_{2} \xrightarrow{} X \xrightarrow{} V$$

$$(D^{+}, Q_{2}^{-}] \xrightarrow{[M^{+}, X^{-}]} O_{2}^{-} + D^{++} \xrightarrow{BET} D + O_{2}^{+}$$

Scheme 5. Proposed interactions of  $O_2$  and salt  $[M^+,X^-]$  with the CIP  $[D^{*+},X^{*-}]$  formed following photoinduced electron transfer between donor (D) and acceptor (X).

feasible (Scheme 5).<sup>[14–16]</sup> Therefore, according to Scheme 4, addition of salts to these reactions is expected to increase the lifetime of the initially formed radical cation ( $D^{++}$ ) due to the suppression of BET by means of metal-induced dismutation of  $O_2^{--}$  (Scheme 5). However, this assumption has never been directly tested before.

To verify the validity of this proposal (Scheme 5), we have examined for the first time the influence of oxygen concentration on the kinetic decay of various radical cations in the presence of metal ion by using laser flash photolysis (LFP) coupled with kinetic absorption spectroscopy. Also, the influence of metal-ion concentration on the kinetic of radical cations has been investigated. In addition, the effect of the type of the metal ion used on the kinetic decay of radical cations has been studied. Furthermore, the factors that affect the stabilities of radical cations have been discussed. The structures of carotenoids and other compounds used in this study are given in Figure 1.

#### Results

Influence of different metal ions on the ground-state spectra of the carotenoids: Carotenoids are lipophilic pigments that are responsible for the color of many vegetables and animals. They are characterized by long conjugated double bonds, which result in a strong absorption in the visible region.<sup>[17]</sup> The absorption maxima ( $\lambda_{max}$ ) and the molar absorption coefficients ( $\varepsilon$ ) for the carotenoids under investigation are given in Table 1.

For astaxanthin (ASTA),  $\lambda_{max} = 495$  nm, there is no significant change in its spectrum in the presence of Li<sup>+</sup>, Na<sup>+</sup>, and NH<sub>4</sub><sup>+</sup> ions in benzonitrile. On the other hand, in the presence of certain metals (e.g., Mn<sup>2+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>, Ni<sup>2+</sup>, Mg<sup>2+</sup>, Lu<sup>3+</sup>, Sc<sup>3+</sup>, and Al<sup>3+</sup>), there is a red shift in its UV/Vis spectrum, and this shift is dependent on the type of metal ion

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Figure 1. Structures of carotenoids and other compounds used in this study.

Table 1. The absorption maxima  $(\lambda_{max})$  for CAR and CAR<sup>+</sup> and the molar absorption coefficients ( $\varepsilon$ ) for CAR in benzonitrile.

CAR	$\lambda_{\max}$ (CAR) [nm]	$\epsilon \ [10^4 \ \text{m}^{-1} \text{cm}^{-1}]^{[a]}$	$\lambda_{\max}$ (CAR <sup>+</sup> ) [nm]
ASTA	495	8.41 <sup>[b]</sup>	880
CAN	490	9.88	880
β-CAR	470	11.64 <sup>[b]</sup>	980

[a]  $\varepsilon$  of CAR at  $\lambda_{max}$  in benzonitrile. [b] Taken from ref. [18].



Figure 2. The influence of scandium-ion concentration on the ground-state spectra of ASTA  $(1 \times 10^{-5} \text{ M})$  in a 1 cm path-length cell.

used (Figure 2 and Figures S1 and S2 in the Supporting Information). The largest shift has been observed in the presence of Sc<sup>3+</sup> ions ( $\lambda_{max}$ =539 nm), which is employed as Sc(OTf)<sub>3</sub> (Figure 2).

These observations clearly indicate that ASTA reacts with the latter metal ions to form metal complexes. According to the literature,<sup>[19,20]</sup> the complex formation is achieved through the chelation of metal ion through the oxygen atoms on the cyclohexene rings (Scheme 6). Furthermore,



Scheme 6. Formation of the ASTA $-M^{n+}$  complex.

the formation constant (*K*) for the complex between  $Sc^{3+}$ ions and ASTA was determined in benzonitrile as  $(4.94 \pm 0.50) \times 10^6 M^{-2}$  using a modified Benesi–Hildebrand equation [Equation (S4) in the Supporting Information; Figure 2 and Figure S4B in the Supporting Information]. Also, the linear plot observed in Figure S4B clearly indicates that the stoichiometry of the ASTA–Sc<sup>3+</sup> complex is 1:2.

On the other hand, CAN and  $\beta$ -CAR, unlike ASTA, do not show any significant spectral change in their ground-state spectra following the addition of various metal ions.

Influence of metal ions on ASTA<sup>•+</sup>: LFP (355 nm) of a solution of  $5 \times 10^{-3}$  M 1,4-dicyanonaphthalene (14DCN) and 0.3 M biphenyl (BP) in air-saturated benzonitrile results in the formation of biphenyl radical cation, BP<sup>•+</sup>, through fast ET quenching of the singlet excited state of 14DCN (Scheme 7).



Scheme 7. Proposed pathways following photolysis of BP and 14DCN in the presence of electron donor (D) and  $O_2$ .

The absorption spectrum of BP<sup>++</sup> (Figure S5 in the Supporting Information), which exhibits two distinct absorption bands in the visible region at 380 and 680 nm, is similar to that reported previously by Lew et al. for BP<sup>++</sup> in oxygen-saturated acetonitrile.<sup>[21]</sup> The 1,4-dicyanonaphthalene radical anion (14DCN<sup>--</sup>), which is characterized by a strong band at 390 nm and a weak band at approximately 500 nm, does not interfere with the observed kinetics, since it is rapidly quenched by oxygen ( $k = 1.3 \times 10^{10} \text{ m}^{-1} \text{ s}^{-1}$ ).<sup>[22–25]</sup> Furthermore, it is important to note that laser photolysis (355 nm) of solutions of 14DCN and BP in air-saturated benzonitrile in the presence or absence of metal ions does not give rise to any transient absorption features in the NIR region.

Following LFP (355 nm) of a solution of  $5 \times 10^{-3}$  M 14DCN and 0.3 M BP in air-saturated benzonitrile that contained  $1 \times 10^{-4}$  M ASTA, a strong NIR absorption around 880 nm at-

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tributed to astaxanthin radical cation (ASTA<sup>+</sup>) was observed (Figure 3 and Scheme 7). This transient spectrum (Figure 3) is in good agreement with that observed following



Figure 3. Transient spectra obtained following LFP (355 nm) of a solution of 14DCN ( $5 \times 10^{-3}$  M) in air-saturated benzonitrile containing BP (0.3 M) and ASTA ( $1 \times 10^{-4}$  M).

ASTA oxidation with  $Br_2^{-}$  [Eq. (1)] in aqueous 2% Triton X-100 ( $\lambda_{max} = 875 \text{ nm}$ ).<sup>[26]</sup> Also, the ET reaction from ASTA to BP<sup>++</sup> is supported by the fact that the oxidation potential of BP ( $E_{ox} = 1.96$  V versus SCE in acetonitrile) is significantly higher than those reported for all carotenoids investigated in this study ( $E_{ox} < 0.9$  V versus SCE in various solvents).<sup>[27,28]</sup> In addition, no transient absorption features have been observed in the NIR region following laser irradiation (355 nm) of air-saturated benzonitrile solutions that contain any of the carotenoids investigated in this study.

$$Br_2^{\bullet-} + ASTA \rightarrow 2Br^- + ASTA^{\bullet+}$$
 (1)

The influence of metal ions on ASTA<sup>++</sup> in air-saturated benzonitrile, generated as described earlier, has been investigated. Figure 4 shows that the lifetime of ASTA<sup>+</sup> is strongly dependent on the identity of the metal ion used. Since the kinetic decay of ASTA<sup>++</sup> in the presence of metal ions is complicated, the half-life of ASTA<sup>++</sup> ( $t_{1/2}$ ) has been taken as a qualitative measure to compare the influence of various metal ions on the stability of ASTA<sup>++</sup>. Figure 4A and Figure S6 in the Supporting Information show clearly the remarkable effect of Mn<sup>2+</sup> on the stability of ASTA<sup>++</sup>. For example, in the presence of  $Mn^{2+}$  ions (as  $Mn(ClO_4)_2$ ), which induces the strongest effect of all the metal ions under investigation, the half-life ( $t_{1/2} \approx 30 \text{ ms}$ ) of ASTA<sup>++</sup> is three orders of magnitude higher than that formed in the absence of the metal ions ( $t_{1/2} \approx 14 \,\mu s$ ). To the best of our knowledge, no similarly substantial effect has been reported for the influence of metal ions on the stabilities of radical cations.

According to half-life measurements (Figure 5), the influence of metal ion on the stability of ASTA<sup>++</sup> can be divided into three categories. The first category, which includes  $Mn(ClO_4)_2$  (or  $Mn(OTf)_2$ ),  $Ni(ClO_4)_2$ ,  $Lu(OTf)_3$ , and  $Ca(ClO_4)_2$  (or  $Ca(OTf)_2$ ), shows a strong effect on the stability of ASTA<sup>++</sup> (Figure 4A). The second category, which includes  $Sc(OTf)_3$ ,  $Zn(ClO_4)_2$  (or  $Zn(OTf)_2$ ),  $Mg(ClO_4)_2$ ,



Figure 4. Influence of 0.002 M of different salts (A, salts with strong effect; B, salts with moderate to weak effect; and C, salts with very weak effect) on the kinetic decay of ASTA<sup>++</sup> at 900 nm generated following LFP (355 nm) of a solution of 14DCN ( $5 \times 10^{-3} \text{ M}$ ) in air-saturated benzonitrile containing BP (0.3 M) and ASTA ( $1 \times 10^{-4} \text{ M}$ ). For comparison, the kinetic absorption profile of ASTA<sup>++</sup> in the absence of salts was added to each plot.



Figure 5. The influence of various metal ions on the half-life  $(t_{1/2})$  of ASTA<sup>++</sup> at 900 nm in air-saturated benzonitrile. The inset shows the influence of various metal ions on the half-life  $(t_{1/2})$  of ASTA<sup>++</sup> on shorter timescales.

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Al(ClO<sub>4</sub>)<sub>3</sub>, NH<sub>4</sub>ClO<sub>4</sub>, LiClO<sub>4</sub>, and NaClO<sub>4</sub> has a moderate to weak effect on the stability of ASTA<sup>++</sup> (Figure 4B).<sup>[29]</sup> Finally, the last group, which includes tetra-n-butylammonium perchlorate (TBAClO<sub>4</sub>) and tetra-n-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>), shows a very weak effect on the stability of ASTA<sup>+</sup>. Therefore, it can be concluded that TBA<sup>+</sup>, PF<sub>6</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> have a very weak influence on the stability of ASTA<sup>++</sup> (Figure 4C). This is in agreement with previous results, which showed that the perchlorate anion has almost no effect on the kinetics of stilbene radicalcation derivatives.<sup>[31]</sup> Furthermore, the influence of metal ions (e.g., Mn(ClO<sub>4</sub>)<sub>2</sub> and Sc(OTf)<sub>3</sub>) on the transient spectrum of ASTA<sup>++</sup> has been investigated. From Figures S7 and S8 in the Supporting Information, it is clear that there is no significant change in the transient spectrum of ASTA<sup>+</sup> in the presence of these salts within the timescale used in these experiments.

Furthermore, the influences of  $Mn(ClO_4)_2$  and  $Mn(OTf)_2$ on the transient absorption profiles of ASTA<sup>++</sup> have been investigated. It is clear that the kinetics of ASTA<sup>++</sup> are not significantly changed in the presence of either  $Mn(ClO_4)_2$  or  $Mn(OTf)_2$  (Figure S9 in the Supporting Information). In addition, similar results were also obtained for the influence of other metal perchlorate and triflate (e.g.,  $Ca^{2+}$  and  $Zn^{2+}$ ions) on the decay of ASTA<sup>++</sup> (see Figures S10 and S11 in the Supporting Information). Consequently, perchlorate or triflate salts of a certain metal ion can both be used with equal success to investigate its role on the stability of CAR<sup>++</sup>.

In addition, the influence of metal-ion concentration on the kinetics of ASTA<sup>++</sup> in air-saturated benzonitrile was investigated. Mn(ClO<sub>4</sub>)<sub>2</sub> was chosen to examine the effect of the metal-ion concentration because of its remarkable effect on the stability of ASTA<sup>++</sup>. At low metal-ion concentrations ( $\leq 1 \times 10^{-5}$  M), there is little change in the kinetics of ASTA<sup>++</sup> . However, at higher concentrations ( $> 1 \times 10^{-5}$  M), the lifetime of ASTA<sup>++</sup> is significantly increased (Figure 6 and Figure S12 in the Supporting Information).

Laser photolysis (355 nm) of solutions of  $5 \times 10^{-3}$  M 14DCN, 0.3 M BP,  $1 \times 10^{-4}$  M ASTA, and 0.002 M Mn(ClO<sub>4</sub>)<sub>2</sub> in benzonitrile in the presence of various oxygen concentrations shows a substantial effect of the oxygen concentration



Figure 6. The influence of  $Mn^{2+}$  concentration, used as  $Mn(ClO_4)_2$ , on the kinetics of ASTA<sup>+</sup> at 900 nm in air-saturated benzonitrile.



Figure 7. The influence of oxygen concentration in the presence of  $Mn(ClO_4)_2$  (0.002 M) on the kinetics of ASTA<sup>++</sup> at 900 nm in benzonitrile.

on the stability of ASTA<sup>++</sup> (Figure 7 and Figure S13 in the Supporting Information). At oxygen concentrations of 5% or higher, the transient absorption profiles of ASTA<sup>++</sup> at 900 nm, show almost similar kinetic behavior. However, at lower oxygen concentration, the decay of ASTA<sup>+</sup> is greatly accelerated. The influence of oxygen on the stability of ASTA<sup>+</sup> in the presence of the other first-category metal ions (Lu<sup>3+</sup>, Ni<sup>2+</sup>, Ca<sup>2+</sup>), which show a strong effect on the stability of ASTA<sup>++</sup>, was also examined. Figure 8 clearly shows that oxygen plays an essential role in the stabilization of ASTA<sup>++</sup> in the presence of these metal ions (0.002 M). To clarify whether or not metal ions have any role in the stabilization of ASTA<sup>+</sup>, laser photolysis (355 nm) of air- and argon-saturated solutions of  $5 \times 10^{-3}$  M 14DCN, 0.3 M BP, and  $1 \times 10^{-4}$  M ASTA in benzonitrile was carried out. Figure S14 in the Supporting Information clearly shows that in the absence metal ions, there is no stabilization for ASTA<sup>+</sup>, that is, transient profiles of ASTA<sup>+</sup> at 900 nm have almost similar kinetic behavior. This clearly indicates that both oxygen and metal ions are essential to the creation of substantial stabilization for ASTA<sup>++</sup>. Also, these results give the first direct observation of the role of oxygen in the special salt effect, which was previously proposed by Astruc's group (Scheme 4).<sup>[2,10-12]</sup>

**Influence of metal ions on CAN<sup>++</sup> and β-CAR<sup>++</sup>**: Laser irradiation (355 nm) of air-saturated solutions of  $5 \times 10^{-3}$  M 14DCN and 0.3 M BP in benzonitrile in the presence of  $7 \times 10^{-5}$  M of various carotenoids (CAN and β-CAR) resulted in the formation of CAN<sup>++</sup> ( $\lambda_{max}$ =880 nm) and β-CAR<sup>++</sup> ( $\lambda_{max}$ =980 nm) (see Figure 9A and B, respectively). In addition, in the absence of oxygen, the kinetics of CAN<sup>++</sup> and β-CAR<sup>++</sup> are not significantly changed (see, for example, Figure S15 in the Supporting Information). The influences of various metal ions on CAN<sup>++</sup> and β-CAR<sup>++</sup> stabilities were studied. Figures S16 and S17 in the Supporting Information show that metal ions behave in a similar way to that observed with ASTA<sup>++</sup>.

In addition, similar results to that of ASTA<sup>++</sup> were observed for the influence of metal-ion and oxygen concentrations on the stabilities of CAN<sup>++</sup> and  $\beta$ -CAR<sup>++</sup> (Figures S18–S23 in the Supporting Information). On the other hand, whereas Mn<sup>2+</sup> ions show substantial effects on the sta-

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Figure 8. Transient profiles of ASTA<sup>++</sup>, at 900 nm, in air- or argon-saturated benzonitrile in the presence of 0.002 M A) Mn<sup>2+</sup>, B) Ni<sup>2+</sup>, C) Lu<sup>3+</sup>, or D) Ca<sup>2+</sup>. For comparison, the kinetic absorption profile of ASTA<sup>++</sup> in the absence of metal ions, in air-saturated benzonitrile, was added to each plot. For a colored version of this figure, see the Supporting Information.

ASTA<sup>+</sup> 90 ms) and  $(t_{1/2})$  $\approx$  30 ms) (Figure 5, Figures S24 and S25 in the Supporting Information). By comparing the structures of these carotenoids, it is clear that the only feature that distinguishes ASTA and CAN from β-CAR is the presence of heteroatoms, oxygen atoms, in their structural formulas (Figure 1). This suggests that the presence of heteroatom plays a role in the stabilization of CAR++, possibly by means of metal-ion-heteroatom interactions.

Furthermore, as shown in Figure 8 and Figures S21 and S23 in the Supporting Information, there is some stabilization of CAR<sup>++</sup> in argon-saturated solutions in the presence of salts relative to those formed in the absence of salts. This



Figure 9. Transient spectra obtained following LFP (355 nm) of 14DCN ( $5 \times 10^{-3}$  M) and BP (0.3 M) in air-saturated benzonitrile containing A) CAN ( $7 \times 10^{-5}$  M) or B)  $\beta$ -CAR ( $7 \times 10^{-5}$  M).

bilities of CAN<sup>++</sup> and  $\beta$ -CAR<sup>++</sup>, as illustrated in Figure 10 and Figures S16A, S17A, S18, and S19 in the Supporting Information, their stabilization effects on  $\beta$ -CAR<sup>++</sup> ( $t_{1/2} \approx 3 \text{ ms}$ ) are still weaker than those observed with CAN<sup>++</sup> ( $t_{1/2} \approx$ 

stabilization can be attributed to the salt interactions with CIP. In accordance with these observations, some radical cations were reported to have some stabilization in the presence of  $Mg^{2+}$  ions in argon-saturated acetonitrile.<sup>[31,32]</sup>



Figure 10. Transient profiles of solutions of A) CAN<sup>++</sup> (at 890 nm) or B)  $\beta$ -CAR<sup>++</sup> (at 980 nm) in air- or argon-saturated benzonitrile containing 0.002 M Mn(ClO<sub>4</sub>)<sub>2</sub>. For comparison, the kinetic absorption profiles of CAN<sup>++</sup> or  $\beta$ -CAR<sup>++</sup> in the absence of metal ions and in air-saturated benzonitrile were added to plots A and B, respectively.

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Since BP<sup>++</sup> is the precursor of CAR<sup>++</sup>, it was important to examine the influence of metal ions on its kinetics. Figures S26 and S27 in the Supporting Information show that the lifetime of BP<sup>++</sup> increases slightly in the presence of Mn-(ClO<sub>4</sub>)<sub>2</sub> (0.002 M). A similar increase in the lifetime of BP<sup>++</sup> was reported in the presence of various salts.<sup>[33]</sup> However, by comparing the influence of Mn<sup>2+</sup> ions on CAR<sup>++</sup> and BP<sup>++</sup> (Figures 8A, 10 and Figures S6, S26 in the Supporting Information), it can be concluded that the overall metal-ion interactions with BP<sup>++</sup> are not responsible for the remarkable effects observed on the stabilities of CAR<sup>++</sup>.

Influence of metal ions on other electron donors: In this part, different electron donors (D) other than carotenoids were investigated to examine the influence of Mn<sup>2+</sup> ions and oxygen on the stabilities of their radical cations  $(D^{\cdot+})$ . Laser photolysis (355 nm) of air-saturated solutions of 14DCN and BP in benzonitrile in the presence of various electron donors (14DPB, 16DPH, 4MeOSt, and trans-St) gave rise to their corresponding radical cations (14DPB<sup>++</sup>, 16DPH<sup>++</sup>, 4MeOSt<sup>++</sup>, and *trans*-St<sup>++</sup>) (Figure 11). The transient spectra of 14DPB'+, 16DPH'+, 4MeOSt'+, and trans-St<sup>++</sup> are in good agreement with the previously reported spectra of these radical cations (Figure 11).<sup>[33-39]</sup> The calculated free-energy change ( $\Delta G$ ) for the ET reactions between BP<sup>++</sup> and various D,  $\lambda_{max}$  values of D<sup>++</sup>, and the oxidation potentials  $(E_{ox})$  of D are noted in Table 2. Moreover, the transient absorption profiles of D<sup>++</sup> show similar kinetic behavior in air- and argon-saturated benzonitrile (Figure S28 in the Supporting Information). Furthermore, it is important to note that laser irradiation (355 nm) of solutions of D alone in air-saturated benzonitrile does not give any transient (or very weak transient) absorption at the  $\lambda_{max}$  of their



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Table 2. Oxidation potentials $(E_{ox})^{[a]}$ , $\lambda_{max}$ of electron-donor radical cati-
ons (D <sup>++</sup> ), and free-energy change ( $\Delta G$ ) for the electron-transfer reac-
tions between BP <sup>++</sup> and various electron donors (D).

D	$\lambda_{\max}$ of D <sup>++</sup> [nm]	$E_{\rm ox}$ [V]	$\Delta G  [ ext{kcal mol}^{-1}]$
14DPB	560	1.21 <sup>[41]</sup>	-17.30
16DPH	600	$1.02^{[39]}$	-21.68
4MeOSt	500	$1.18^{[35]}$	-17.99
trans-St	480	1.52 <sup>[39]</sup>	-10.15

[a] Oxidation potentials  $(E_{ox})$  were measured against SCE in acetonitrile.

corresponding radical cations  $(D^{+})$  (Figures S29–S31 in the Supporting Information).<sup>[40]</sup>

In a similar trend to that observed with CAR, 14DPB<sup>++</sup>, 16DPH<sup>++</sup>, and 4MeOSt<sup>++</sup> show significant stabilization in the presence of oxygen and  $0.002 \,\mathrm{M} \,\mathrm{Mn}(\mathrm{ClO}_4)_2$  (Figure 12A-C). Again, these results confirm that oxygen and certain metals interact cooperatively to induce remarkable effects on the stabilities of the radical cations. On the other hand, trans-St<sup>++</sup> shows little stabilization in the presence of 0.002 M Mn(ClO<sub>4</sub>)<sub>2</sub> (Figure 12D and Figure S32 in the Supporting Information). Furthermore, in the presence of the metal ion, the observed kinetics are hardly affected by the absence of oxygen, which suggests that oxygen has almost no influence on the stabilization of trans-St+ (Figure 12D). Comparing the influence of Mn<sup>2+</sup> ions on trans-St<sup>++</sup> with that of 4MeOSt<sup>++</sup> again raises the possibility of the involvement of metal-ion-heteroatom interactions in the stabilization of 4 MeOSt<sup>+</sup>.

Furthermore, the transient spectrum of BP<sup>++</sup> overlaps with the transient spectra of D<sup>++</sup>, therefore it is important to compare the transient absorption profiles of D<sup>++</sup> with that of BP<sup>++</sup> under the same experimental conditions. Figures S33–S36 in the Supporting Information clearly reveal that

> BP<sup>++</sup> absorption interferes very little with the observed kinetics of D<sup>++</sup> at their  $\lambda_{max}$  value. In addition, the intensity of the transition absorption profile of BP<sup>++</sup> observed in the absence of D will be significantly reduced in the presence of various electron donors on account of its quenching by these electron donors.

#### Discussion

In light of these results and the work of Astruc's group, the principal steps that show the role of oxygen in the presence of salts  $[M^{n+},X^{-}]$  in photoinduced ET reactions are described in Scheme 8. Photolysis of 14DCN in the presence of BP and various electron donors

Figure 11. Transient spectra obtained following LFP (355 nm) of solutions of 14DCN ( $5 \times 10^{-3}$  M) and BP (0.3 M) in air-saturated benzonitrile containing A) 14DPB ( $1 \times 10^{-4}$  M) (laser energy = 13 mJ), B) 16DPH ( $7 \times 10^{-5}$  M), C) 4MeOSt ( $1 \times 10^{-3}$  M), or D) *trans*-St ( $1 \times 10^{-3}$  M).

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Figure 12. Transient profiles of solutions of A) 14DPB<sup>++</sup> (at 560 nm), B) 16DPH<sup>++</sup> (at 600 nm), C) 4MeOSt<sup>++</sup> (at 500 nm), or D) *trans*-St<sup>++</sup> (at 480 nm) in air- or argon-saturated benzonitrile containing 0.002 M Mn(ClO<sub>4</sub>)<sub>2</sub>. For comparison, the kinetic absorption profiles of 14DPB<sup>++</sup>, 16DBH<sup>++</sup>, 4MeOSt<sup>++</sup>, or *trans*-St<sup>++</sup> in the absence of metal ions, and in air-saturated benzonitrile were added to plots A, B, C, and D, respectively. For a colored version of this figure, see the Supporting Information.



Scheme 8. The influence of  $O_2$  and salt  $[M^{n+},X^-]$  on the different transient intermediates formed following photolysis of 1,4-dicyanonaphthalene (14DCN) and biphenyl (BP) in the presence of electron donor (D).

(D) results in the formation of 14DCN<sup>--</sup> and D<sup>++</sup> (Scheme 8, pathway i). In the presence of oxygen, 14DCN<sup>--</sup> reacts rapidly  $(k = 1.3 \times 10^{10} \text{ m}^{-1} \text{ s}^{-1})^{[25]}$  with O<sub>2</sub> to form O<sub>2</sub>. (pathway ii). This ET reaction from 14DCN<sup>--</sup> ( $E_{ox} = -1.31$  V versus SCE in acetonitrile)<sup>[42,43]</sup> to oxygen  $(E_{\rm red} = -0.86 \text{ V})$ versus SCE in acetonitrile)<sup>[44]</sup> is thermodynamically feasible  $(\Delta G = -10.4 \text{ kcal mol}^{-1})$ . In the presence of  $[M^{n+}, X^{-}]$ , O<sub>2</sub><sup>-</sup> reacts with the metal ion to form the corresponding metalion-superoxo complexes  $[(M^{n+})(O_2^{\cdot})]$  (Scheme 8, pathway iii). Once formed, these metal-ion-superoxo complexes, which were reported to be transiently stable, dismute to oxygen and peroxide as described in Scheme 8 (pathways iv and v).  $^{[45-54]}$  Overall, the inhibition of BET from  $O_2^{\, \cdot -}$  to the radical cation (Scheme 8, pathway vii) is mainly due to metal-induced dismutation of  $O_2^{-}$ , that is, the degree of BET inhibition depends mainly on the superoxide dismutase (SOD) activity of the metal ions.<sup>[55]</sup>

It is important to note that the complex formation between metal ion and  $O_2^{\bullet-}$ (Scheme 8, pathway iii) is based on the results of many reports about the ability of  $O_2$ <sup>-</sup> to react with various metal ions (e.g., Li<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Zn<sup>2+</sup>, Tl<sup>+</sup>, Ba<sup>2+</sup> Cd<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Y<sup>3+</sup> Sc<sup>3+</sup>, Lu<sup>3+</sup>, and Cr<sup>3+</sup>) to form metal-ion-superoxo complexes  $[(M^{n+})(O_2^{\cdot-})]$ .<sup>[45-53,56,59]</sup> Also, the formation of metal-ion-superoxo complexes was reported to promote thermodynamically unfavorable electrontransfer reactions between oxygen and various electron donors.<sup>[60]</sup> In addition, the binding energies of many metal ions with  $O_2^{-}$  have been evaluated.<sup>[56,61,62]</sup>

It is also noteworthy that, in addition to BET (Scheme 8, pathways vi and vii), other reactions such as isomerization, deprotonation. dimerization. and addition reactions (Scheme 8, pathway viii) can compete for the decay of D<sup>++</sup> .<sup>[63]</sup> The contribution of these reactions to the decay of D<sup>++</sup> is dependent on their relative rate constants. Therefore the weak effects of metal ions on the stabilities of BP++ and trans-St<sup>++</sup> (Figure 12D and Figures S26, S27 in the Supporting Information), in the presence

of oxygen, can be partly attributed to the presence of other major pathways (Scheme 8, pathway viii) available for the decay of these radical cations, which is to say, BET is not the major pathway for their decay.

Furthermore, the dependence of the kinetic decay of CAR<sup>++</sup> on metal concentration (Figure 6 and Figures S18, S19 in the Supporting Information) in the presence of oxygen can be attributed to the shift in the equilibrium of the ion-exchange reaction (see Scheme 8, pathway iii) toward the formation of  $[D^{++},X^{-}]$  and  $[(M^{n+})(O_2^{-+})]$ , which leads to the retardation of BET.<sup>[2]</sup>

It should be noted that the enhancement of the transient absorption intensity of CAR<sup>++</sup> and D<sup>++</sup> observed in the presence of salts can be accounted for by the ionic environment induced by the salts, which stabilizes the radical ion formation (see Figures 6, 8, 12, and Figures S18 and S19 in the Supporting Information). There are many examples in the literature<sup>[9,19,32,33,64]</sup> that showed an increase in the yield of radical ions following the addition of salt.

In addition, the significant increase in the stability of heteroatom-containing radical cations (HA<sup>++</sup>) (see CAN<sup>++</sup> versus  $\beta$ -CAR<sup>++</sup> and 4MeOSt<sup>++</sup> versus *trans*-St<sup>++</sup>) has been attributed to metal-ion-heteroatom interactions. The occurrence of such interactions might facilitate the presence of metal ions near HA<sup>++</sup>, which results in the efficient disproportionation of O<sub>2</sub><sup>--</sup> before undergoing BET to HA<sup>++</sup>.<sup>[65]</sup>

Of special interest is the influence of  $Mn^{2+}$  ions on the stability of  $\pi$ -conjugated radical cations. Manganese is an essential element for many physiological processes because of its role in the activity of many enzymes, for example, managanese superoxide dismutase (MnSOD).<sup>[66–68]</sup> The well-known reactivity of MnSOD toward  $O_2^{--}$  has drawn much attention toward the investigation of the reactivity of Mn<sup>2+</sup> ions toward  $O_2^{--}$ .<sup>[51–53,69,70]</sup> Pulse radiolysis studies established that Mn<sup>2+</sup> ions react rapidly with  $O_2^{--}$  to form a short-lived manganous-superoxide transient species  $[(Mn^{2+})(O_2^{--})]$ ,<sup>[71]</sup> which decays along various pathways depending on the nature of the anion used.<sup>[51–53,70]</sup> For example, in the presence of phosphate as an anion,  $[(Mn^{2+})(O_2^{--})]$  disproportionates rapidly to form manganous phosphate, oxygen, and hydrogen peroxide (Scheme 9, pathway i). On the other



Scheme 9. Various pathways for the decay of manganese-superoxo complex.

hand, if Mn<sup>2+</sup> ions are bound to pyrophosphate, the  $[(Mn^{2+})(O_2^{-})]$  decay results in the formation of manganic pyrophosphate and hydrogen peroxide (Scheme 9, pathway ii).<sup>[53]</sup> Therefore, in light of these results, it is reasonable to suggest that the substantial effects induced by Mn<sup>2+</sup> ions on the stability of most of the investigated  $\pi$ -conjugated radical cations can be attributed to the efficient scavenging of  $O_2^{-}$  by  $Mn^{2+}$  ions, which results in the inhibition of the BET reaction. To the best of our knowledge, the influence of Mn<sup>2+</sup> ions on photoinduced ET reactions has not previously been examined. However, the influence of other salts such as Mg(ClO<sub>4</sub>)<sub>2</sub>, NaClO<sub>4</sub>, LiClO<sub>4</sub>, KClO<sub>4</sub>, LiBF<sub>4</sub>, and others on various reactions have been reporte $d.^{[3,6a,7,9,10,31-33,36]}$  Since  $Mn^{2+}$  ions show a remarkable effect on the kinetics of radical cations, it will be of interest to reexamine some of these reactions in the presence of Mn<sup>2+</sup> ions.

### **FULL PAPER**

#### Conclusion

The conclusions that arise from the work reported in this manuscript are as follows: 1) the direct observation of the role of oxygen in the special salt effect is reported for the first time; 2) many parameters are important in determining the stability of radical cation: the nature of the metal ion, the nature of the radical cation, metal-ion and oxygen concentrations, and relative contributions of the other competitive pathways to the decay of the radical cation; 3) the anions used (i.e., ClO<sub>4</sub><sup>-</sup> and TfO<sup>-</sup>) in this study have little effect on the stabilization of the radical cation; 4) for heteroatom-containing radical cations, the heteroatom does seem to have a significant effect on the stabilization of the radical cation; 5) according to our results, the significant stabilization of radical cation observed in air-saturated solutions that contained metal ions can be attributed to the cooperative interaction between O2<sup>--</sup> and metal ions to prevent the BET from  $O_2^{-}$  to the radical cation; 6) the manganese ion, which is a biologically relevant metal ion, shows a substantial ability to stabilize radical cations. This ability can be directly attributed to its well-known SOD activity observed either as a part of SOD enzymes or as free metal ions.[45,46,51-53,67,68]; and 7) generation of carotenoid radical cations by laser photolysis of 14DCN and BP in the presence of CAR can be used as a basis for a new method of screening the relative SOD activities of various metal ions.

We are currently extending these results to study the influence of manganous phosphate, which was reported to remove rapidly and catalytically O2- from aqueous solutions,<sup>[53]</sup> and other salts on the stability of various radical cations in biologically relevant environments, for example, aqueous Triton X-100. In addition, many CAR<sup>++</sup> are able to oxidize various biological molecules such as tyrosine and cysteine and this reaction can cause deleterious effects, for example, enzyme inactivation, if it occurs in vivo.[28,72] Therefore, it is important to re-examine the reactivity of CAR'+, in the presence of metal ions, toward these molecules to shed light about the influence of metal ions on these reactions. Finally, the role induced by the presence of heteroatom in the structure of radical cations will be further studied by investigating the influence of metal ions on various radical cations and their corresponding heteroatom-containing radical cations.

#### **Experimental Section**

**Materials**: 1,4-Diphenyl-1,3-butadiene, 1,6-diphenyl-1,3,5-hexatriene, calcium perchlorate tetrahydrate, calcium triflate, scandium triflate, zinc perchlorate hexahydrate, zinc triflate, manganese perchlorate hydrate, manganese triflate, aluminium perchlorate nonahydrate, lutetium triflate, biphenyl (99.5%), and benzonitrile (99.9%) were purchased from Aldrich. Sodium perchlorate (anhydrous) and magnesium perchlorate were purchased from Wako. *trans*-Stilbene, 1,4-dicyanonaphthalene (98%), and tetra-*n*-butylammonium perchlorate were purchased from Tokyo Chemical Industry (TCI). Nickel perchlorate hexahydrate (STREM CHEMICALS), 4-methoxy-*trans*-stilbene (fluorochem), lithium perchlo-

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GaA, Weinheim www.chemeurj.org \_\_\_\_\_9 These are not the final page numbers! rate (anhydrous, Nacalai Tesque), ammonium perchlorate (Nacalai Tesque), astaxanthin (Alexis Biochemicals,  $\geq 97\%$ ), and  $\beta$ -carotene (Fluka,  $\geq 97\%$ ) were used as received. Canthaxanthin was kindly supplied by Dr. David J. McGarvey (School of Physical and Geographical Sciences, Keele University, Keele, Staffordshire ST5 5BG, UK) and was used as received. Argon (99.99\%) was supplied by Yamazaki Sangyo, Japan. A gas blender (GB-3C) from KOFLOC, Japan, was used to obtain various oxygen concentrations.

Laser flash photolysis experiments: For the nanosecond-laser flash photolysis experiments, solutions were excited by a Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) at 355 nm. Time courses of the transient absorption spectra were measured using a continuous Xe lamp (150 W) and an In GaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded using fresh solutions following each exposure to the laser. Quartz sample cells (5 mm excitation path length ×10 mm monitoring path length) were employed for the laser flash photolysis measurements. Saturated solutions of argon and various oxygen concentrations were performed at 298 K. The laser energy used was  $\leq 4$  mJ unless otherwise stated. The standard errors in the measurements are  $\pm 10\%$  unless otherwise stated.

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### CHEMISTRY

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#### **Radical Cations -**

- Left The Remarkable Effect of the Manganese Ion with Dioxygen on the Stability of π-Conjugated Radical Cations

 $\mathbf{A}^{+} \mathbf{D} \xrightarrow{h\nu} \mathbf{A}^{+} \mathbf{D}^{+}$   $\downarrow^{O_2} \xrightarrow{} \mathbf{A}^{+} \mathbf{D}^{+}$   $\downarrow^{O_2} \xrightarrow{} \mathbf{A}^{+} \mathbf{D}^{+}$   $\downarrow^{(\mathbf{M}^{n+})(O_2^{-})] \xrightarrow{} \mathbf{O}_2^{+} \mathbf{D}^{+}$   $\downarrow^{[(\mathbf{M}^{n+})(O_2^{-})]}$   $\mathbf{M}^{n+} + \mathbf{O}_2 + [(\mathbf{M}^{n+})(O_2^{-})]$ 

Life changes: Mn ions show a substantial effect on the lifetime of  $\pi$ -conjugated radical cations (D<sup>++</sup>) in the presence of oxygen (see scheme). However, this remarkable effect is greatly diminished if either oxygen or manganese ions are removed from the solution. These observations can be attributed to the inhibition of the back electron transfer between O<sub>2</sub><sup>--</sup> and D<sup>++</sup>.