(Pt_2) shoulders are attributable to $^3(p\sigma \leftarrow d\delta^*)$.

The emission that is observed for $M_2(dppm)_3$ is assumed to arise from the $^3A_2''$ excited state. Spin-orbit coupling probably controls the emission lifetimes ($\tau_e(Pd) > \tau_e(Pt)$; Table I); it also manifests itself in the intensities of the weak absorptions associated with transitions to the spin triplets ($Pt_2 > Pd_2$).

The solid-state resonance Raman spectra of $M_2(dppm)_3$ are shown in Figure 4. Peaks attributable to metal-metal stretching vibrations are at 120.0 (Pd_2) and 102.5 cm^{-1} (Pt_2). Woodruff's equations[18] relating bond distance (r/Å) and force constant (F/mdyn Å^{-1}) for M_2 complexes of the 4d and 5d series are shown in eq 1 and 2. We obtain r = 3.024 Å for $Pt_2(dppm)_3$, which is in good agreement with the published value (3.025 Å).[14] No crystallographic data exist for $Pd_2(dppm)_3$; eq 1 estimates the metal-metal separation to be 3.043 Å. The force constant in $Pd_2(dppm)_3$ (0.45 mdyn Å^{-1}) is smaller than the one in $Pt_2(dppm)_3$ (0.60 mdyn Å^{-1}), thereby indicating that weaker metal-metal interactions occur. The blue shift of the singlet $p\sigma \leftarrow d\sigma^*$ band from Pt_2 to Pd_2 also suggests that the M-M interaction is weaker in the Pd_2 complex.

$$r(4d) = 1.83 + 1.45 \exp(-F/2.53) \qquad (1)$$

$$r(5d) = 2.01 + 1.31 \exp(-F/2.36) \qquad (2)$$

Excitation in $^1(p\sigma \leftarrow d\sigma^*)$ yields two Raman peaks in the 20-200-cm^{-1} region, one metal-metal stretch (in agreement with the assignment of the electronic transition) and one P-M-P 50-60-cm^{-1} bend. Because of the strongly allowed character of the electronic band, the latter mode presumably is totally symmetric.

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Cis and Trans Olefin Radicals: Equilibrium and Photoisomerization

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Abstract: Electrochemical reduction of 1,2-bis(1-methyl-4-pyridino)ethylene dication gives the same reduction potentials (−0.53 and −0.72 V vs SCE in CH_3CN) for both cis and trans isomers. Only the absorbance spectrum of the trans radical (ϵ(max) 57 000 M^{-1} cm^{-1} at 517 nm) is observed. However, by using pulse radiolysis the radicals of both cis and trans isomers are observed in aqueous solution. Although their absorbance spectra are similar, the extinction coefficients are very different. The cis radical is intrinsically stable but undergoes rapid electron exchange with the trans dication isomer. Cis and trans radicals equilibrate through electron exchange, the limiting rate constants in both directions of the equilibrium being 2×10^9 M^{-1} s^{-1} (cis to trans) and 3×10^8 M^{-1} s^{-1} (trans to cis). The photoisomerization of the olefin radicals is essentially one-way: the quantum yield for the cis radical is 0.2, while that of the trans is less than 0.01.

Little is known about the photoisomerization of olefin radicals. The first suggestion that it might occur comes from the observations by Shida and Hamill during their study of stilbene cation spectra in solid matrices.[1] Study of the photoisomerization of olefin radicals in solution requires detection and spectral characterization of both cis and trans radical isomers. Furthermore, the temporal stability of these radicals must be ascertained to allow for photolysis.

The existence of distinct cis and trans isomeric radical cations of stilbene in solid matrices was shown by Shida and Hamill.[1] Later Szwarc and co-workers proved in a series of papers that, contrary to past belief, even in solution the cis radical anion of stilbene is long-lived and has distinct properties from the trans radical anion.[2,3] Perhaps because of the complexity of the reactions observed and of the failure of identifying cis radical isomers for other olefins,[4] it is still believed that cis radical isomers of olefins cannot be observed in solution due to their very short lifetimes or simply because they do not exist.[5-7]

To address the considerations just cited, this study first establishes the distinct properties of cis and trans radicals of the olefin 1,2 bis(1-methyl-4-pyridinio)ethylene, BPE^{2+},[8] whose structures are shown in Figure 1. Then by means of a pulse radiolysis-flash photolysis setup, the photoisomerization of the olefin radicals is examined.

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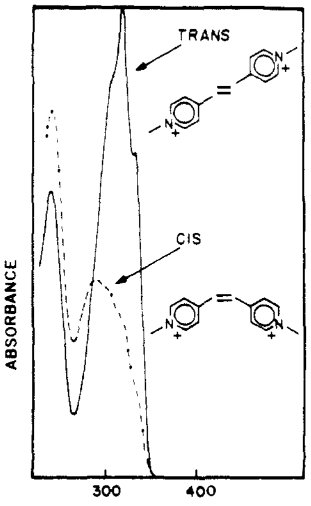

Figure 1. Absorbance spectra of *cis*- (---) and *trans*-$BPE^{2+}(I^-)_2$ (—) in acetonitrile.

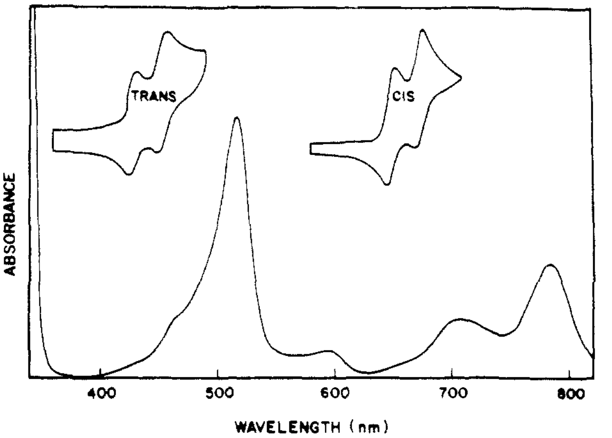

Figure 2. Cyclic voltammograms of *cis*- and *trans*-BPE^{2+} in acetonitrile between 0 and −1.0 V (200 mV/s, 0.1 M TBAP). Absorbance spectrum of *trans*-$BPE^{\bullet+}$ obtained by electrochemical reduction in CH_3CN.

Experimental Section

The picosecond pulse radiolysis equipment,[9] the nanosecond pulse radiolysis apparatus,[10,11] and the combined pulse radiolysis–flash photolysis technique[12] have been described elsewhere. The pulse radiolysis experiments were done in aqueous solutions containing 0.01 M $LiClO_4$ and 0.04 M *tert*-butyl alcohol, under N_2 atmosphere unless otherwise indicated. The transient radical concentrations in the pulse radiolysis experiments were $<10^{-5}$ M. The cyclic voltammetry and coulometry were carried out in acetonitrile with 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte, degassed with argon. Platinum electrodes were used. The spectra were recorded with a Cary 219. *cis*- and *trans*-$BPE^{2+}(I^-)_2$ were prepared according to the method already described elsewhere.[8] It was found to be very difficult to obtain trans-free cis isomers after quaternarization with CH_3I. The cis isomer will isomerize to trans in the dark at low ionic strength, further complicating the preparation. However, the fraction of residual trans in the cis preparations used in this study was always less than 0.1.

Results

1. Properties of Cis and Trans Radicals. The absorbance spectra of *cis*- and *trans*-$BPE^{2+}(I^-)_2$, together with their structures, are given in Figure 1. The maximum extinction coefficients are 42 000 M^{-1} cm^{-1} at 316 nm for trans and 15 600 M^{-1} cm^{-1} at 288 nm for cis. BPE^{2+} being very electron deficient, it is easily reduced. In the next paragraphs electrochemical and pulse radiolytic results are presented that establish the properties of the cis and trans isomers in their reduced form.

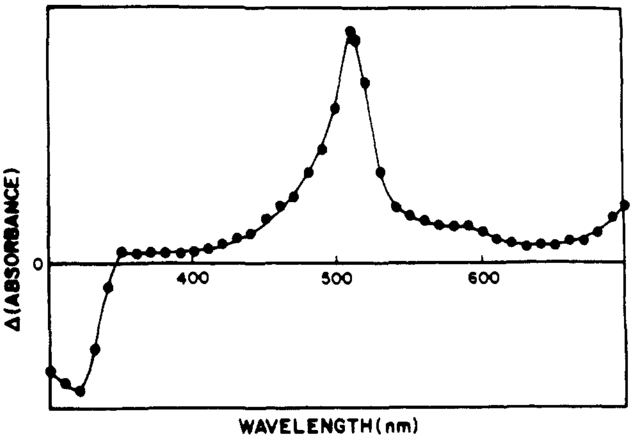

Figure 3. Differential absorbance spectrum observed after reduction of *trans*-BPE^{2+} by pulse radiolysis ($[trans\text{-}BPE^{2+}(I^-)_2] = 2 \times 10^{-5}$ M).

Electrochemical Reduction. The cyclovoltammograms (CV) of both cis and trans isomers are very similar (Figure 2) and give the same redox potentials within experimental error: $E_1 = -0.53$ V (vs SCE), $E_2 = -0.72$ V (vs SCE). Only at low scan rates (e.g., 10 mV/s) and under O_2 saturation do the CV become irreversible. From the dependence of the CV reversibility on the scan rate (in the presence of O_2), it appears that the reaction of the $BPE^{\bullet+}$ with O_2 in CH_3CN is very slow. This was confirmed when quantitative coulometry was undertaken to determine the spectra of the reduced product(s) of BPE^{2+}. After reduction under argon, a purple solution was obtained, which was very insensitive to O_2 with a half-life of the order of 5 min as measured with a spectrophotometer. The reaction between O_2 (in excess) and trans radical was not a pseudo-first-order reaction as expected. Starting with either cis or trans isomer, the spectrum of the reduced species was the same and is given in Figure 2. The maximum extinction coefficient is 57 000 M^{-1} cm^{-1} at 517 nm.

From the above results, it could be concluded that both cis and trans isomers give just one radical species (or at least just one stable radical), most likely the trans radical isomer. So a set of picosecond and nanosecond pulse radiolysis experiments were undertaken with the aim of trying to detect a distinct cis radical entity.

Pulse Radiolytic Reduction. First picosecond experiments were carried out with the expectation that the cis radical isomer would be very short-lived. However, to our surprise cis radical isomer is very stable and long-lived, as will be evident from the following results.

Figure 3 shows the differential absorbance spectrum obtained after the solvated electron has reacted with *trans*-BPE^{2+} in water. It is identical with the spectrum that was found after electrochemical reduction (Figure 2). The peak at ~515 nm has an extinction coefficient of 59 000 M^{-1} cm^{-1}, very similar to that obtained in CH_3CN. The spectrum can be assigned to *trans*-$BPE^{\bullet+}$. Both cis and trans isomers of BPE^{2+} react with the aqueous electron with a diffusion-controlled rate (reactions 1 and 2), where k^t and k^c have the same value, 6×10^{10} M^{-1} s^{-1}, within

$$trans\text{-}BPE^{2+} + e_{aq}^- \rightarrow trans\text{-}BPe^{\bullet+} \qquad k^t \qquad (1)$$

$$cis\text{-}BPE^{2+} + e_{aq}^- \rightarrow cis\text{-}BPE^{\bullet+} \qquad k^c \qquad (2)$$

experimental error (15%), as determined by observing the rate of disappearance of the solvated electron.

The differential spectrum observed in the case where reaction 2 is the main pathway is, however, very different (see Figure 4, dashed curve). Furthermore, this initial spectrum then changes into the solid curve spectrum in Figure 4, which resembles the trans radical spectrum. The rate of this spectral change was found to depend on both [*cis*-BPE^{2+}] and [*trans*-BPE^{2+}] and follows

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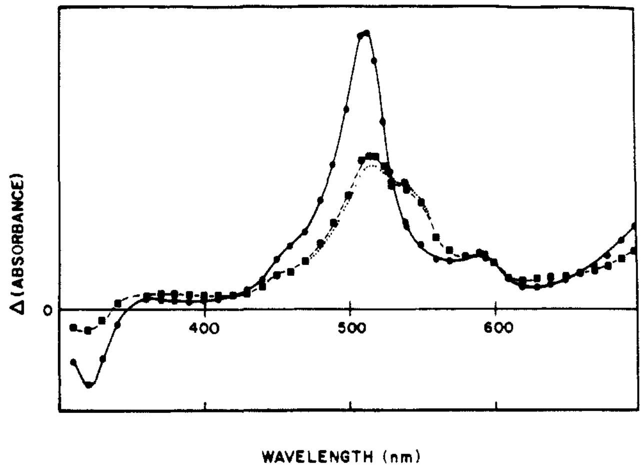

Figure 4. Differential absorbance spectra observed after reduction of *cis*-BPE^{2+} (3.6×10^{-4} M) and *trans*-BPE^{2+} (0.4×10^{-4} M) by pulse radiolysis. Initial spectrum (---) and final spectrum (–) of an equilibrated mixture of cis and trans radicals. The dotted line is that of *cis*-$BPE^{\cdot +}$ alone.

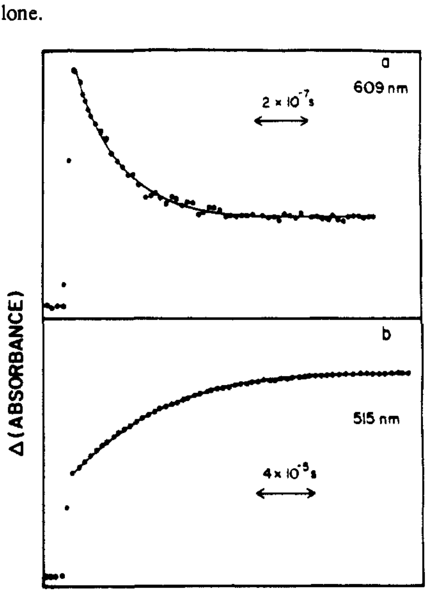

Figure 5. (a) Reaction of *cis*-BPE^{2+} (10^{-4} M) with solvated electron. (b) Electron-exchange reaction from cis to trans isomers ([*cis*-BPE^{2+}] = 3.6×10^{-4} M, [*trans*-BPE^{2+}] = 0.4×10^{-4} M).

pseudo-first-order kinetics. These observations can only be explained by a charge-transfer equilibrium as shown in reaction 3,

$$cis\text{-}BPE^{\cdot +} + trans\text{-}BPE^{2+} \overset{K}{\rightleftharpoons} cis\text{-}BPE^{2+} + trans\text{-}BPE^{\cdot +} \quad (3)$$

where the equilibrium constant K is determined by the reduction potential difference of *trans*- and *cis*-BPE^{2+}. K is equal to the ratio of the rates in the two directions of equilibrium 3.

Examples of the successive reactions 2 and 3 are shown in Figure 5a,b. The final spectrum in Figure 4 (solid curve) resembles that of the trans radical, but it is not pure; it represents the equilibrium mixture of cis and trans radicals at a given set of concentrations for the species in reaction 3. The initial spectrum in Figure 4 is 90% that of the cis radical isomer and 10% that of trans. The spectrum of the cis radical alone is given by the dotted line in Figure 4. Compared with the trans radical spectrum, the major difference is in the extinction coefficients. Just like the parent isomers (Figure 1), the cis radical maximum extinction coefficient is much smaller. The absorbance peak is roughly at the same wavelength as that of the trans radical. The maximum extinction coefficient of *cis*-$BPE^{\cdot +}$ is 26 000 M^{-1} cm^{-1}; this value was obtained by comparing with the known extinction coefficients of the aqueous electron.[14]

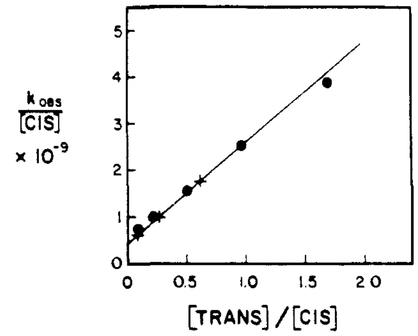

Figure 6. Kinetic analysis of the electron-exchange equilibrium between cis and trans isomers (see text). Key: (+) variation of [*cis*-BPE^{2+}] between 1.4×10^{-4} and 8×10^{-4} M, [*trans*-BPE^{2+}] = 8.0×10^{-5} M; (●) variation of [*trans*-BPE^{2+}] between 4.0×10^{-5} and 6.5×10^{-4} M, [*cis*-BPE^{2+}] = 3.6×10^{-4} M.

Having identified both *cis*- and *trans*-$BPE^{\cdot +}$, it is possible to analyze equilibrium 3. The rate constant in both directions can be determined by measuring the observed pseudo-first-order rate constant k_{obsd} for various concentrations of *cis*- and *trans*-BPE^{2+}, since it is well-known that in such a case[13] $k_{obsd} = k_1$[*trans*-BPE^{2+}] + k_{-1}[*cis*-BPE^{2+}]. By plotting k_{obsd}/[*cis*-BPE^{2+}] vs [*trans*-BPE^{2+}]/[*cis*-BPE^{2+}], a straight line is expected with slope k_1 and intercept k_{-1}. This is shown in Figure 6, and k_1 is 2×10^9 M^{-1} s^{-1} and k_{-1} is 3×10^8 M^{-1} s^{-1}. From the ratio we find that the kinetically measured equilibrium constant K of reaction 3 is 7. There is a large inherent error in determining k_1 and k_{-1} when the system is close to equilibrium, as has been shown by Benson.[15]

Therefore, K was also determined by analyzing the equilibrium mixture of the two radical isomers for various concentrations of *cis*- and *trans*-BPE^{2+}. This can be done since the extinction coefficients of both cis and trans radical isomers have been measured. The value of K estimated this way is 30 (±10). The difference in K obtained by the two methods can be due either to the large inherent error margins or because the equilibrium involves an intermediate complex. For the latter to be true, one would expect to observe the intermediate. However, we were unable to detect it, indicating a large error margin in our results. Therefore, the redox potentials difference of the cis and trans isomers is somewhere between 50 and 87 mV, as determined from these values of K.

It should be noted that no intrinsic isomerization of the cis radical isomer could be detected. Only an upper limit for the intrinsic isomerization rate could be estimated from our experiments; $<10^4$ s^{-1}. Evidently, in the absence of trans isomer and therefore reaction 3, the *cis*-$BPE^{\cdot +}$ is very stable. Furthermore, no other reactions (e.g., dimerization) were observed for either radical.

Finally, the reaction between cis and trans radical isomers and O_2 was observed in water. The rate constants for both radicals had the same value within experimental error: $4 \pm 1 \times 10^8$ M^{-1} s^{-1}. The reactivity is thus considerably higher in water than in acetonitrile. This will be discussed later.

2. Radical Photoisomerization. Having determined the spectral identity of both trans and cis radical isomers and the kinetics of electron exchange (reaction 3), the photochemistry of the radicals could now be investigated. By use of a combined pulse radiolysis–flash photolysis experimental setup, the radical was first produced with a short electron pulse. Then a dye laser, tuned to an absorption band of the radical, excited the radical with a certain delay after its formation.

Conveniently, the cis and trans radical have high extinction coefficients at 520 nm (Figure 4) where the parent isomers do not absorb (Figure 1). This wavelength was then used to excite the radicals, 4 μs after their formation. This is illustrated in Figure 7 for both cis and trans isomers. While for the trans radical no photochemistry was observed (Figure 7a), a significant absorbance

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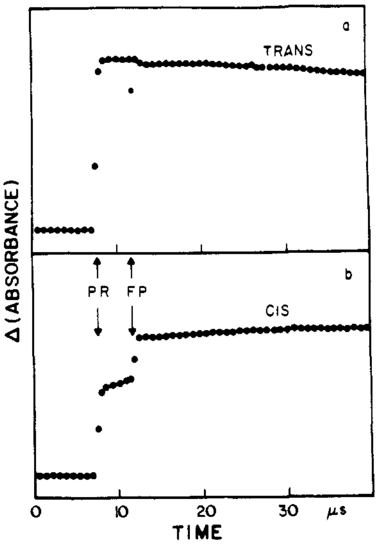

Figure 7. Combined pulse radiolysis (PR) and flash photolysis (FP) experiments. ([BPE^{2+}(I$^-$)$_2$] $\simeq$ 10^{-4} M; laser intensity at 520 nm = 10^{-7} einstein cm^{-2}). (The dip after FP for trans is due to light scattering.)

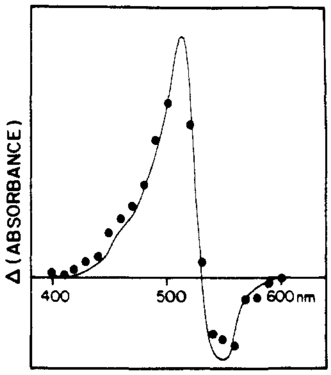

Figure 8. Differential absorbance (●) after excitation of *cis*-BPE$^{\bullet+}$ at 520 nm. Solid curve: calculated differential spectrum of *cis*-BPE$^{\bullet+}$ and *trans*-BPE$^{\bullet+}$ (ϵ(*trans*-BPE$^{\bullet+}$) − ϵ(*cis*-BPE$^{\bullet+}$)) normalized to the experimental point at 500 nm.

change was observed after excitation of the cis radical (Figure 7b). These absorbance changes between 400 and 600 nm, shown in Figure 8, are in very good agreement with the calculated differential spectra of cis and trans radicals (solid curve, Figure 8). It is thus clear that the cis radical photoisomerizes while trans does not, to any measurable degree. The radical photoisomerization quantum yields were found to be 0.2 for cis and less than 0.01 for trans, using the comparative method[16] with zinc tetraphenylporphyrin triplet absorbance in cyclohexane as reference ($\epsilon_T\phi_T \approx 50\,000$ M^{-1} cm^{-1} at 470 nm).[17]

Discussion

Although cis and trans radical isomers of BPE^{2+} spectra resemble each other, they can clearly be distinguished. The two radical isomers will equilibrate through electron exchange with the parent dications. Intrinsic (intramolecular) isomerization is very slow, if it occurs at all. Qualitatively, these properties are similar to those of the stilbene radical anions reported by Szwarc and his co-workers.[3] However, the present study is not complicated by secondary reactions such as dimerization and disproportionation. The stability of BPE$^{\bullet+}$ is probably due to the strong electron deficiency of the parent compound BPE^{2+}.

It is interesting to note that the electrochemical experiments did not reveal any detectable difference in the redox potential of cis and trans isomers, although the pulse radiolysis results indicate it should be about 50–85 mV. Whitten and his co-workers also found identical CV for both cis and trans isomers.[4] This apparent contradiction between the pulse radiolysis and the electrochemical results could perhaps be explained by reaction 3 if the samples are not ultra pure, or by surface phenomena on the platinum electrode, which are faster than the time resolution of the electrochemical apparatus. Pulse radiolysis is thus clearly better suited for analyzing radical isomers.

It seems that the electron-exchange reactions that lead to apparent, but no net, isomerization of radicals are quite common.[18] So unless the samples are very pure or the time resolution is high, the high-energy isomer will be observed even if it is intrinsically stable. This is probably why Whitten and his co-workers were unable to detect *cis*-BPE$^{\bullet+}$ using conventional flash photolysis, despite carefully planned experiments.[4] Other effects such as cis–trans isomerization catalyzed by intermediates generated in the photolysis might also make the cis radical isomer more difficult to detect.

The reactivity of the BPE$^{\bullet+}$ radicals with O$_2$ is surprisingly sensitive to the solvent. In aqueous solution, a pseudo-first-order reaction is observed as expected when O$_2$ is in excess compared with the radical species, the bimolecular rate constant being 4×10^8 M^{-1} s^{-1}. In acetonitrile, the kinetics appear to be second order even in the presence of excess O$_2$, and they are very slow (first half-life is on the order of minutes). Such solvent dependency has been observed and analyzed in detail for other bipyridinium salts by Evans and his co-workers.[19] It has been demonstrated that in certain solvents the reaction between a bipyridinium radical and O$_2$ proceeds through two steps. First the radical and O$_2$ form a complex, which then reacts with another radical. Depending on the temperature, this second step is the limiting one and in such cases explains the second-order nature of the kinetics. Our results fit such an explanation and indicate that this behavior must be quite general for bipyridinium radicals.

The mixed pulse radiolysis–flash photolysis experiments unambiguously establish the photoisomerization of olefin radicals. However, within the experimental resolution, the radical photoisomerization appears only to occur in one direction from cis to trans. It should be noted that this is similar to the one-way photoisomerization of anthrylethylenes[20,21] via the triplet state, although the role of unpaired electron remains undefined. Clearly, the potential surface of the excited radical, as a function of angle of rotation around the double bond, does not have the simple features of ethylene with a minimum in the twisted geometry such as with the parent BPE^{2+}.[22] More studies of olefins will be necessary to gain further insight into the effect of unpaired electrons on the potential surfaces.

Conclusion

It has been shown that radicals generated from cis and trans isomers of BPE^{2+} are distinct species. The cis radical isomer is intrinsically stable but will disappear rapidly in the presence of *trans*-BPE^{2+} due to electron transfer to the latter. It is clear that unless time-resolved techniques are used (e.g., pulse radiolysis), cis olefin radicals and their properties will be difficult to determine in solution due to reactions such as electron exchange. Radical photoisomerization upon direct excitation has been observed in solution at room temperature. The photoisomerization of the olefin is essentially one way from cis to trans radical.

Acknowledgment. We are indebted to S. Nelsen (University of Wisconsin) and G. Ferraudi (University of Notre Dame) for

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Registry No. *cis*-BPE$^{2+}\cdot 2I^-$, 101342-61-4; *trans*-BPE$^{2+}\cdot 2I^-$, 24274-78-0; BPE$^{\bullet+}$, 46740-62-9; O_2, 7782-44-7.

Carotenoid Cation Radicals: Electrochemical, Optical, and EPR Study

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Abstract: Cyclic voltammetry, absorption spectroscopy, and electron paramagnetic resonance spectroscopy (EPR) have been employed to study the production of carotenoid cation radicals via electrochemical means in various solvents [tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and dichloroethane ($C_2H_4Cl_2$)]. The electrooxidation of purified β-carotene, β-apo-8′-carotenal, and canthaxanthin in THF was found to proceed via a two-electron process. In the chlorinated solvents, the oxidation of β-carotene again occurred by the transfer of two electrons; in contrast, however, β-apo-8′-carotenal and canthaxanthin were oxidized via the transfer of only one electron. In all cases the apparent number of electrons transferred was found to be strongly dependent on the purity of the carotenoids. Electronic absorption measurements showed that the products generated at the first anodic peak potential have intense absorptions in the near-infrared (IR). Literature reports have shown that the only carotenoid oxidation products that absorb in this spectral region are carotenoid cations and cation radicals. EPR measurements of the electrooxidized products showed single-line spectra with a g value (2.0026) typical of hydrocarbon cation radicals. Furthermore, the oxidized β-carotene solutions exhibited an EPR line width of ~14 G, which is consistent with the value determined by second moment calculations of the β-carotene cation radical monomer. This is conclusive evidence that the electrochemical oxidation of carotenoids produces cation radicals. The one-electron oxidation of both β-apo-8′-carotenal and canthaxanthin directly results in the production of these radicals; however, the two-electron oxidation of β-carotene produces dications, which are believed to react with the neutral species to produce the cation radical, according to $C + C^{2+} \rightarrow 2C^{\bullet+}$ (where C = β-carotene). The stability of the carotenoid cation radicals was shown to be highly solvent dependent, with the β-carotene cation radical exhibiting the longest lifetime in CH_2Cl_2.

Carotenoid compounds are present in the chloroplasts of photosynthetic green plants and are essential for the plants' survival. The role of the carotenoids is believed to be twofold:[1-4] (1) they serve as photoproduct devices by preventing the formation of damaging singlet oxygen; (2) they act as antenna pigments for the absorption of light energy in the spectral region where chlorophyll is not an efficient absorber; they then transfer this energy to chlorophylls for the performance of photosynthesis.

Carotenoids are also thought to play another role in the photosynthetic process. Although the exact location of the carotenoids within the photosynthetic membrane has not yet been determined, it is known that they are in close association with the chlorophyll-containing PSII reaction center.[5,6] Because of this close association and also because of their extended conjugated systems (β-carotene has 11 double bonds), evidence for carotenoid-mediated redox reactions has been sought. Mathis and his coworkers[7,8] recently reported that light excitation of chloroplasts produces absorption changes due to formation of a carotenoid cation radical at the PSII reaction center.

Light-driven electron-transport processes across membranes are essential to the development of artificial photosynthetic systems that would convert solar energy into chemical energy. Recent work by Moore et al.[9-11] has shown that molecular triad molecules consisting of porphyrins covalently linked to both carotenoids and quinones (C–P–Q) can achieve photodriven electron transfers in good yield. Excitation of the C–P–Q moiety yields the porphyrin first excited singlet state C–^{1}P–Q, which donates an electron to the quinone to form C–P$^{\bullet+}$–Q$^{\bullet-}$. A second electron-transfer reaction yields a final charge-separated state C$^{\bullet+}$–P–Q$^{\bullet-}$, which in solution has a lifetime on the order of microseconds. This evidence further suggests that carotenoids can play an active role in the photosynthetic electron-transport chain. Moreover, the carotenoid cation radical C$^{\bullet+}$ appears to be an integral part of the electron-transfer process, and it follows that detailed knowledge of the carotenoids and their oxidation products is important to the overall understanding of these processes.

The oxidation of carotenoids has been previously studied by photochemical,[7,8,12] radiolytic,[13-15] and chemical means.[16-20]

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