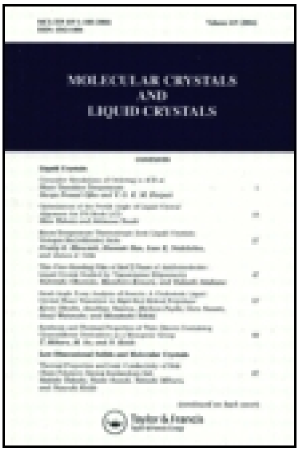

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SPECIFIC INTERACTION OF 4-NITROSTYRYLPYRIDINIUM IONS UPON PHOTOEXCITATION IN SOLUTIONS

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Abstract Ion-pair charge-transfer complexes of 4-nitrostyrylpyridinium with tetraphenylborate as its counter ion gave fairly stable styrylpyridinyl radicals in 1,2-dimethoxyethane at room temperature due to photoinduced electron transfer reactions between ion pairs. In addition to the remarkable colour changes due to a characteristic absorption of styrylpyridinyl radicals in the visible region, a charge resonance (CR) band was also observed in the near infrared region. The CR band indicated specific interaction of photogenerated neutral radicals with their parent styrylpyridinium cations. Prolonged irradiation and/or storage in the dark after irradiation caused further colour changes depending on the initial concentrations and irradiation times. These results indicated that nitrostyrylpyridinyl radicals had stronger tendency of association in the dark.

INTRODUCTION

We have been studying photochemical and photophysical properties of ion-pair charge-transfer (IPCT) complexes in various microenvironments.[1-9] By the use of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as a counter ion of 4,4'-bipyridinium ion, we have achieved novel photochromism due only to the photoinduced electron transfer and thermal reverse reactions in solutions and in polymer or Langmuir-Blodgett films.[1-5] The ultrafast colour changes in less than 20 ps were observed in polymer films by ps laser photolysis.[6,7] We have also reported novel second harmonic generation (SHG) from IPCT complexes and its photochemical control,[8] and very recently for the first time the charge resonance (CR) band due to the electronic interaction between a photogenerated radical and a parent cation using substituted styrylpyridinium tetraphenylborate salts by steady photolysis in 1,2-dimethoxyethane (DME) solutions at room temperature.[9]

We now report the specific interactions of nitrostyrylpyridinyl radicals formed by photoinduced electron transfer reactions of 1-octadecyl-4-(4-nitrostyryl)pyridinium tetraphenylborate in solutions.

EXPERIMENTAL

1-Octadecyl-4-(4-nitrostyryl)pyridinium (abbreviated to NS^+) bromide was synthesized according to the similar method reported previously.[8,9] Its counter ion was exchanged with tetraphenylborate (abbreviated to TPB^-) using Na^+TPB^- to obtain pale-yellow crystals of an NS^+TPB^- salt. The purity was confirmed by NMR, elemental analysis, and fluorescence spectroscopy. The structures of both ions are shown in Figure 1.

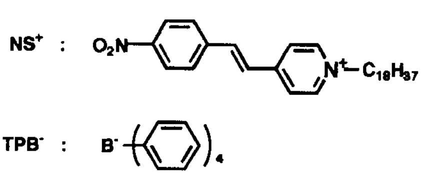

FIGURE 1 Molecular structure and abbreviation of nitrostyrylpyridinium tetraphenylborate.

The absorption spectra were observed by a Hitachi U-3500 UV-VIS-NIR spectrophotometer before and after irradiation *in vacuo* by a Hamamatsu 150 W Xe-Hg lamp through an L-39 cut-off filter (λ_{ex} > 365 nm) and an IR-cut-off filter. The ESR spectra were measured with a JEOL JES-RE1X spectrometer during and after irradiation at room temperature.

RESULTS AND DISCUSSION

Upon irradiation with a Xe-Hg lamp (λ_{ex} > 365 nm) the colour of DME solutions first changed from pale-yellow to pink or pale-red. New absorptions were observed both in the visible and near infrared (NIR) region. The difference absorption spectra of a 0.5 mmol dm^{-3} DME solution of NS^+TPB^- using unirradiated sample as a reference are shown in Figure 2 after four different irradiation times. It shows two peaks in the visible region at about 450 nm and 570 nm and a broad peak at 950 nm. Contrary to the increase of the visible absorption from (c) to (d) in Figure 2, the NIR region band remained almost constant during irradiation for another 30 s and the new absorption at 630 nm appeared as indicated by an arrow. The visible absorption was assigned to 1-octadecyl-4-(4-nitrostyryl)pyridinyl radical that was formed by the photoinduced electron transfer from TPB$^-$ *via* the excited IPCT complex.[9] The reverse electron transfer reaction to oxidized TPB$^-$ is prohibited, because TPB$^-$ is known to decompose after one-electron oxidation.[10] This radical was thus fairly stable and was observed for about 1 h at room temperature.

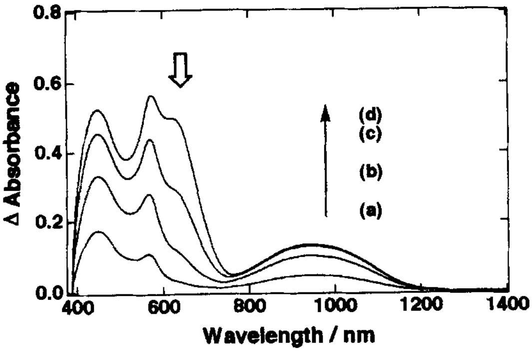

FIGURE 2 The difference absorption spectra of NS$^+$TPB$^-$ in a 0.5 mmol dm^{-3} DME solution after irradiation for (a) 10 s, (b) 30 s, (c) 60 s and (d) 90 s at room temperature. The spectrum before irradiation was used as a reference.

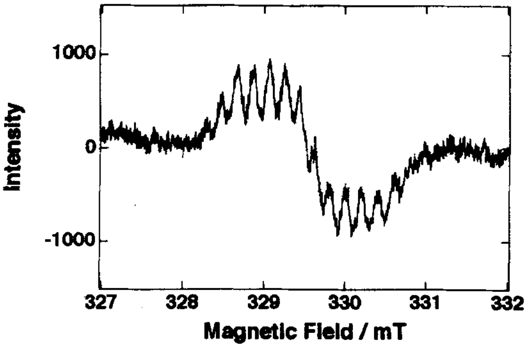

FIGURE 3 The ESR spectrum of NS$^+$TPB$^-$ in a 0.5 mmol dm^{-3} DME solution irradiated for 5 min at 20 °C.

The absorption spectrum in the NIR region with a peak at about 950 nm was attributed to the CR band due to the electronic interaction between a photogenerated 1-octadecyl-4-(4-nitrostyryl)pyridinyl radical and its parent cation.[9] The CR band had been observed for dimer radical cations formed by γ-radiolysis[11,12] and pulse radiolysis[13,14] in rigid matrices at or near 77 °K, and by nanosecond laser flash photolysis[15-20] at room temperature in solution. This was the first CR band observed by steady photolysis at room temperature in solutions.[9] ESR spectra were also observed during and after irradiation *in vacuo* as shown in Figure 3, which were composed of a hyperfine structure with more than 15 lines. The observed spectrum coincided with the calculated one for dimer nitrostyrylpyridinyl radical cations. These signals decayed by second-order kinetics until about 20 min and were observed for about an hour at room temperature.

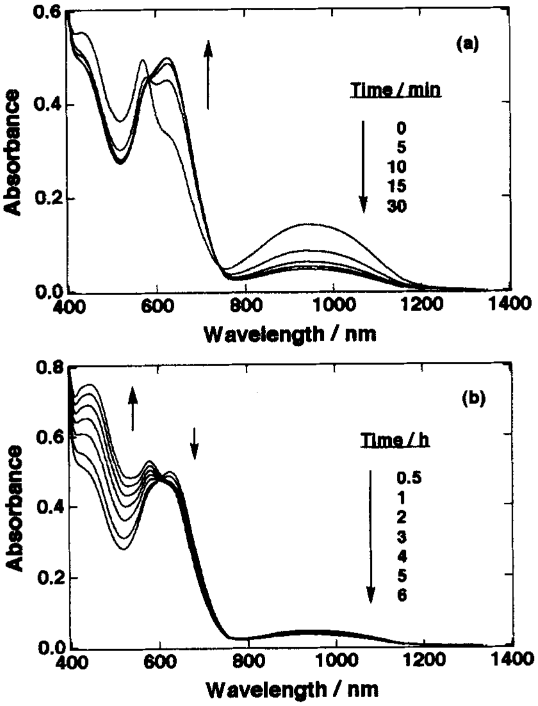

FIGURE 4 Changes of absorption spectra of $NS^{+}TPB^{-}$ during storage (a) until 30 min and (b) after 30 min in the dark after irradiation for 1 min in a 0.5 mmol dm^{-3} DME solution at room temperature.

The storage in the dark at room temperature after irradiation caused further colour changes from pale-red to smoky blue. The spectral changes are shown in Figure 4 for a 0.5 mmol dm^{-3} DME solution. The absorptions of nitrostyrylpyridinyl radical at 570 nm and the CR band in the NIR region decreased. The new absorption with a peak at about 630 nm appeared and increased its intensity until about 30 min after irradiation. The absorption at 630 nm is similar to the band that was appeared by prolonged irradiation as shown in Figure 2. The decay of CR band followed almost second-order kinetics until about 30 min. The absorption spectra in a more dilute 0.05 mmol dm^{-3} DME solution are shown in Figure 5 during storage in the dark at room temperature after irradiation. Although the absorptions of nitrostyrylpyridinyl radical and the CR band were observed similarly as in 0.5 mmol dm^{-3} solutions, the absorption at 630 nm increased only slightly after irradiation. Thus these results strongly suggested that the species at 630 nm results from intermolecular reaction of dimer radical cations. The species at 630 nm can be assigned to J-like aggregates of nitrostyrylpyridinyl radicals. During further storage in the dark at room temperature, the absorption at 630 nm decreased accompanying an increase of absorption in a shorter wavelength region with an isosbestic point at 600 nm in Figure 4 and at 505 nm in Figure 5. This suggests further changes in the structure of aggregates or other reactions, the details of which have not been clarified yet.

From the present results, nitrostyrylpyridinium molecules and nitrostyrylpyridinyl radicals were shown to have stronger tendency of association. The molecular structures of both nitrostyrylpyridinium cation and its reduced form are shown to be planar from MOPAC calculations and a molecular model.[9] Recently Hunter reported that so-called π-π interactions are dominated by electrostatics, which means the most favorable interaction of π-systems is found when the substituents are both strongly electron withdrawing.[21] The nitrostyrylpyridinium ion has two strong electron withdrawing groups, nitro and pyridinium. The nitrostyrylpyridinyl radical has a nitro group. The stronger tendency of association can be expected from such long and planar structures with extensive charge delocalization which favour the electronic interactions.

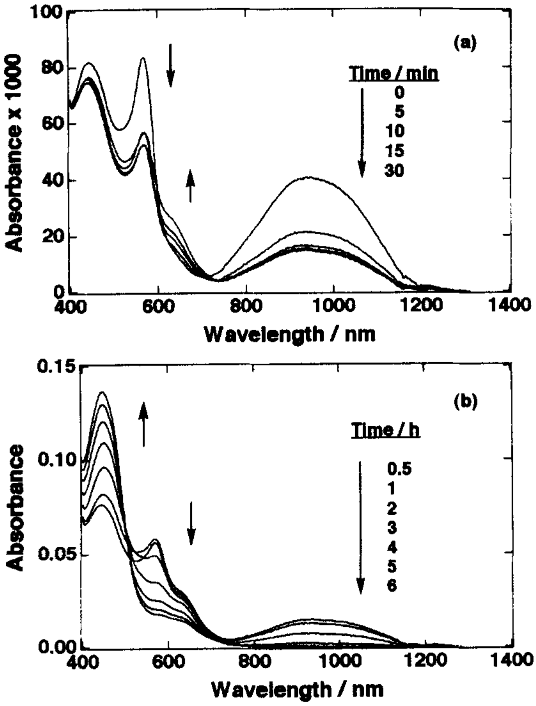

FIGURE 5 Changes of absorption spectra of NS$^+$TPB$^-$ during storage (a) until 30 min and (b) after 30 min in the dark after irradiation for 1 min in a 0.05 mmol dm^{-3} DME solution at room temperature.

CONCLUSION

Photoinduced electron transfer reactions occurred upon excitation of ion-pair charge-transfer complexes of 4-nitrostyrylpyridinium tetraphenylborate in DME solutions at room temperature to form fairly stable styrylpyridinyl radicals. From a CR band and very gradual spectral changes in the dark after irradiation, the nitrostyrylpyridinyl radicals were found to have stronger tendency of association and specific interactions.

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REFERENCES

1. T. Nagamura and K. Sakai, J. Chem. Soc., Chem. Commun., 810 (1986).
2. T. Nagamura and K. Sakai, Chem. Phys. Lett., 141, 533 (1987).
3. T. Nagamura and K. Sakai, Ber. Bunsenges. Phys. Chem., 92, 707 (1988).
4. T. Nagamura and Y. Isoda, J. Chem. Soc., Chem. Commun., 72 (1991).
5. T. Nagamura, Mol. Cryst. Liq. Cryst., 224, 75 (1993) and references cited therein.
6. T. Nagamura, H. Sakaguchi, S. Muta and T. Ito, Appl. Phys. Lett., 63, 2762 (1993).
7. T. Nagamura, H. Sakaguchi, T. Ito and S. Muta, Mol. Cryst. Liq. Cryst., 247, 39 (1994).
8. H. Sakaguchi, T. Nagamura and T. Matsuo, J. Chem. Soc., Chem. Commun., 209 (1992).
9. T. Nagamura, A. Tanaka, H. Kawai and H. Sakaguchi, J. Chem. Soc., Chem. Commun., 599 (1993).
10. P. J. Grisdale, J. L. R. Williams, M. E. Glogoski and B. E. Babb, J. Org. Chem., 36, 544 (1971).
11. B. Badger, B. Brocklehurst and R. D. Russel, Chem. Phys. Lett., 1, 122 (1967).
12. A. Kira, T. Nakamura and M. Imamura, Chem. Phys. Lett., 54, 582 (1978).
13. R. E. Buhler and W. Funk, J. Phys. Chem., 79, 2098 (1975).
14. A. Kira and M. Imamura, J. Phys. Chem., 83, 2267 (1979).
15. M. Yamamoto, Y. Tsujii and A. Tsuchida, Chem. Phys. Lett., 154, 559 (1989).
16. Y. Tsujii, A. Tsuchida, Y. Onogi and M. Yamamoto, Macromolecules, 23, 4019 (1990).
17. Y. Tsujii, A. Tsuchida, S. Ito and M.Yamamoto, Macromolecules, 24, 4061 (1991).
18. A. Tsuchida, Y. Tsujii, M.Ohoka and M. Yamamoto, J. Phys. Chem., 95, 5797 (1991).
19. A. Tsuchida and M. Yamamoto, J. Photochem. Photobiol. A: Chem., 65, 53 (1992).
20. A. Tsuchida, H. Takamura and M. Yamamoto, Chem. Phys. Lett., 198, 193 (1992).
21. C. A. Hunter, Angew. Chem. Int. Ed. Engl., 32, 1584 (1993).