7 March 1997



Chemical Physics Letters 266 (1997) 601-606

CHEMICAL PHYSICS LETTERS

Excited-state dynamics of naphthoylnaphthvalene: valence isomerization of the lowest excited singlet state and intermolecular hydrogen-atom abstraction of the lowest excited triplet state

Toshihiro Nakayama, Tetsuhiko Nagahara, Sadao Miki, Kumao Hamanoue *

Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

Received 19 November 1996; in final form 20 December 1996

Abstract

By measurements of phosphorescence and transient absorption spectra as well as steady-state photolysis of the title compound (NNV), it is concluded as follows: (1) In benzene and ethanol, intersystem crossing from the lowest excited singlet ($^{1}NNV^{*}$) to triplet ($^{3}NNV^{*}$) states competes with valence isomerization of $^{1}NNV^{*}$ yielding ground-state naphthoylnaphthalene (NN). (2) In ethanol, the NNV ketyl radical (generated by hydrogen-atom abstraction of $^{3}NNV^{*}$ from the solvent molecule) also undergoes rapid valence isomerization and recombination of two NN ketyl radicals thus formed yields 1,1,2,2-tetranaphthyl-1,2-ethanediol (naphthopinacol).

1. Introduction

In the context of the recent importance of photoresponsiveness of molecules in the wide range of molecular devices, we are studying the photophysics and photochemistry of polycyclic aromatic compounds which undergo photoinduced valence isomerization yielding the Dewar-type [1-4] or valene-type [4-6] isomers. Owing to the large strain energy and the peculiar sp⁹ hybridization in the bicyclobutane moiety [7], the photochemistry of valene-type compounds is also of great interest and Turro et al. [8] reported that the lowest excited singlet state of naphthvalene underwent valence isomerization forming the lowest excited triplet state of naphthalene; neither population of the lowest excited triplet state of the original compound (naphthvalene) nor formation of the lowest excited singlet state of the photoproduct (naphthalene) was observed.

Generally, intersystem crossing from the lowest excited singlet to triplet states of aromatic carbonyl compounds is very rapid. And, the result reported by Turro et al. [8] has intrigued us with a view of finding out which of the lowest excited singlet and triplet states of valene-type aromatic carbonyl compounds undergo valence isomerization as well as whether the electronically excited products are formed or not. In comparison with the results obtained for naphthoylnaphthalene (NN), therefore, this Letter deals with the excited-state dynamics of naph-

^{*} Corresponding author.

^{0009-2614/97/\$17.00} Copyright © 1997 Elsevier Science B.V. All rights reserved. PII \$0009-2614(97)00047-X

thoylnaphthvalene (NNV). For this compound, a bridgehead carbon atom of the naphthvalene moiety is substituted by the naphthoyl group.

2. Experimental

By the treatment of naphthvalene (prepared following the method of Katz et al. [9]) with n-butyllithium in the presence of N,N,N',N'-tetramethylethvlenediamine, a lithionaphthvalene (with a lithiated bridgehead carbon atom) was obtained at first and then its reaction with 2-naphthaldehyde followed by CrO₃/pyridine oxidation yielded NNV. NN was synthesized by the reaction of 2-naphthyllithium with 2-naphthaldehyde yielding dinaphthylcarbinol followed by successive Jones oxidation. Crude NNV and NN thus obtained, and GR-grade benzophenone (BP) from Wako were recrystallized from diisopropyl ether, ethanol and ligroin, respectively. The solvents used were benzene, ethanol and a mixed solvent (EPA) of diethyl ether/isopentane/ethanol (5:5:2 in volume ratio). Although spectral-grade benzene (Dojin) and Uvasol diethyl ether (Merck) were used without further purification, GR-grade isopentane (Wako) was purified by passing it through an alumina column and spectral-grade ethanol (Nacalai) was dried using a molecular sieve 3A (Wako).

The sample solutions were degassed by several freeze-pump-thaw cycles and nanosecond laser photolysis was performed using the third harmonic [the 355 nm light pulse with a full width at half-maximum intensity (FWHM) of 5 ns] from a Nd³⁺:YAG laser (Continuum Surelight I); the transient absorption spectra were recorded using a multichannel analyzer [10], and the decay curves of transient absorptions as well as the phosphorescence decay curves were analyzed by means of a combination of a photomultiplier (Hamamatsu R329 or R666) with a storage oscilloscope (Iwatsu TS-8123).

Steady-state photolysis was carried out using the 313 nm monochromatic light selected from a USH-500D super-high-pressure mercury lamp, and the absorption and phosphorescence spectra were recorded using a Hitachi 200-20 spectrophotometer and a Hitachi MPF-4 spectrophosphorimeter, respectively.

3. Results and discussion

Fig. 1a shows the phosphorescence spectra obtained for NNV, NN and BP in EPA at 77 K. Clearly, the phosphorescence spectrum (the solid line) obtained for NNV is slightly different from that (the dashed line) obtained for NN but their phosphorescence decay curves can be analyzed by a singleexponential function with a lifetime of and $\tau_{\rm p} = 1$ s. In contrast, the phosphorescence spectrum (the dotted line) and its lifetime ($\tau_{\rm P} = 5.6$ ms) obtained for BP are greatly different from those obtained for NNV and NN. Since the lowest excited triplet state $({}^{3}\text{BP}^{*})$ of BP is well known to be of typical $n\pi^{*}$ character, large π -conjugation between the naphthalene moiety and the carbonyl group of NNV (or NN) compared with that between the benzene moiety and the carbonyl group of BP may be a cause of lowering the $\pi\pi^*$ energy level resulting in the lowest excited triplet states of NNV (³NNV^{*}) and NN $(^{3}NN^{*})$ to be of $\pi\pi^{*}$ or mixed $n\pi^{*}-\pi\pi^{*}$ character. In fact, the $\pi^* \leftarrow \pi$ absorption bands of NNV and NN shift greatly to longer wavelengths compared with that of BP and no $\pi^* \leftarrow n$ absorption bands can be seen for the former compounds.



Fig. 1. (a) Phosphorescence spectra and (b) $T' \leftarrow T_1$ absorption spectra (at 10 ns delay) obtained for NNV, NN and BP in EPA at 77 K. τ_P in (a) are the phosphorescence lifetimes and τ_T in (b) are the lifetimes of $T' \leftarrow T_1$ absorptions.

As shown in Fig. 1b, nanosecond laser photolysis in EPA at 77 K reveals that the transient absorption spectrum (the solid line) obtained for NNV is slightly different from that (the dashed line) obtained for NN but they differ greatly from that (the dotted line) obtained for BP. Furthermore, the lifetime of transient absorption obtained for NNV is equal to that obtained for NN but this lifetime ($\tau_T = 1$ s) is very long compared with that ($\tau_T = 5.6$ ms) obtained for BP. Since these results are consistent with those obtained for the phosphorescence spectra and their lifetimes shown in Fig. 1a, the transient absorption spectra shown in Fig. 1b can safely be assigned to the triplet-triplet ($T' \leftarrow T_1$) absorptions due to ³NNV^{*}, ³NN^{*} and ³BP^{*}.

At room temperature, nanosecond laser photolysis of NNV and NN in benzene also reveals the appearance of $T' \leftarrow T_1$ absorption spectra due to ³NNV^{*} and ³NN^{*} with lifetimes of $\tau_T = 12$ and 15 µs, respectively (cf. Fig. 2), i.e. the corresponding decay rate constants are $k_1 = 8.3 \times 10^4$ and 6.7×10^4 s⁻¹, respectively, and no new transient absorption spectra

INNV

0

:NN

700

τ_T = 15 μs

20 30 40

600

(c) NN

(a)

0.75

0.5

0.25

0.75

0.5

0.25

0

0 10

0

400

(b) NNV

500

= 12 µs

20 30 40

Wavelength / nm

1.2

0.9

0.6

0.3

0

Time / µs

0

10

Absorbance

Fig. 2. (a) $T' \leftarrow T_1$ absorption spectra at 10 ns delay and (b, c) decay curves of transient absorptions (——, monitored at 450 nm) obtained for NNV and NN in benzene at room temperature. In (b) and (c), the dashed curves are the best-fit single-exponential functions with lifetimes (τ_T) indicated.

Fig. 3. Transient absorption spectra obtained for (a) NNV and (b) NN in ethanol at room temperature; delay times are 10 ns (----) and 500 μ s (---).

can be seen during the decrement of $T' \leftarrow T_1$ absorption spectra with time. In ethanol, however, the spectra (the solid lines) obtained at 10 ns delay are identical with the $T' \leftarrow T_1$ absorption spectra due to ${}^3NNV^*$ and ${}^3NN^*$ but the spectra (the dashed lines) obtained at 500 µs delay are clearly different from the $T' \leftarrow T_1$ absorption spectra (cf. Fig. 3). In accordance with this, as shown in Fig. 4, the transient absorptions monitored at 450 nm decrease with time following the first-order and then second-order decay kinetics with rate constants k_1 and k_2 , respectively; for k_2 , ε is the absorption coefficient of a transient species different from ${}^3NNV^*$ or ${}^3NN^*$.

Fig. 5a shows the absorption spectral change caused by steady-state photolysis of NNV in ethanol at room temperature and the photoproduct with absorption bands P_1-P_4 is identified to be NN. In benzene at room temperature, a similar result is also obtained for NNV but no photochemical reaction can be seen for NN; as shown in Fig. 5c, however, photolysis of NN in ethanol at room temperature causes a spectral change different from that shown in Fig. 5a. Meanwhile, Turro et al. [8] observed only the phosphorescence originating from the lowest excited triplet state of naphthalene upon excitation of





Fig. 4. Decay curves of transient absorptions (——, monitored at 450 nm) obtained for (a, b) NNV and (c, d) NN in ethanol at room temperature. The dashed curves are the best-fit ones calculated on the basis of the first-order and second-order decay kinetics with rate constants k_1 and k_2 , respectively; for k_2 , ε is the absorption coefficient of a transient species different from ³NNV* or ³NN^{*}.

naphthvalene in methylcyclohexane at 77 K. On the basis of this fact, as stated previously, they concluded that the lowest excited singlet state of naphthvalene underwent valence isomerization forming the lowest excited triplet state of naphthalene. Formation of the lowest excited singlet (¹NN^{*}) and/or triplet (³NN^{*}) states of NN from the lowest excited singlet state $(^{1}NNV^{*})$ of NNV (or conversion of $^{3}NNV^{*}$ to ³NN^{*}) upon excitation of NNV, however, can be ruled out on the basis of following facts; (1) by excitation of NNV in EPA at 77 K, only the phosphorescence and $T' \leftarrow T_1$ absorption spectra due to ³NNV^{*} can be seen (cf. Fig. 1); (2) steady-state photolysis of NNV in EPA at 77 K also yields NN and the resulting phosphorescence spectrum can be ascribed to the superposition of phosphorescence originating from ³NNV^{*} and ³NN^{*} which are populated by independent excitation of the original compound (NNV) and the photoproduct (NN), respectively; (3) nanosecond laser photolysis of NNV in benzene at room temperature reveals no formation of ³NN *, i.e. only the $T' \leftarrow T_1$ absorption spectrum due to ${}^{3}NNV^{*}$ can be seen (cf. Fig. 2). We have further observed that ³NNV^{*} in aerated benzene at room temperature is quenched by dissolved oxygen ($\approx 1-3$ mM) with a rate constant of $\approx (3.1-1.0) \times 10^9$ M⁻¹ s⁻¹ but steady-state photolysis reveals no effect of oxygen on the rate of formation of NN from NNV. Since no formation of NN is observed by a thermal reaction of NNV, it can be conclude that ¹NNV^{*} undergoes valence isomerization yielding groundstate NN.

A comparison of the result shown in Fig. 5a with that shown in Fig. 5b indicates that the absorption bands (P_1-P_4) of NN produced by photolysis of NNV in ethanol disappear by prolonged photolysis reflecting the occurrence of a photochemical reaction between NN and ethanol. In fact, Fig. 5c indicates that photolysis of NN in ethanol at room temperature causes the absorption spectral change similar to that shown in Fig. 5b and we have confirmed formation of 1,1,2,2-tetranaphthyl-1,2-ethanediol (naph-thopinacol) as the final product. All the results ob-



Fig. 5. Absorption spectral changes upon steady-state photolysis of (a, b) NNV and (c) NN in ethanol at room temperature.

tained by nanosecond laser photolysis as well as steady-state photolysis of NN in ethanol at room temperature are very similar to those obtained for aromatic carbonyl compounds such as benzophenone [11], flavanones [12–14] and 4-chromanone [12,14]: The lowest excited triplet states of these compounds abstract a hydrogen atom from the solvent molecules generating the corresponding ketyl radicals and solvent radicals, and recombination of two ketyl radicals yields the pinacol-type compounds. Naturally, formation of naphthopinacol upon steady-state photolysis of NN in ethanol can be interpreted in terms of recombination of two NN ketyl radicals (NNK⁻). Hence, the dashed spectrum shown in Fig. 3b can be ascribed to the absorption of NNK', because the corresponding spectral intensity decreases with time following the second-order decay kinetics with a rate constant of $k_2 = 3.4\varepsilon \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (cf. Fig. 4d). Interestingly, the dashed spectrum shown in Fig. 3a and the decay curve of transient absorption shown in Fig. 4b are confirmed to be identical with those shown in Figs. 3b and 4d, respectively. This may indicate that the NNV ketvl radical (NNVK') generated by hydrogen-atom abstraction of ³NNV* from ethanol also undergoes rapid valence isomerization resulting in formation of NNK ' (cf. Scheme 1). This conjecture is supported by the well-known facts that rearrangement of cyclopropylcarbinyl radicals to allylcarbinyl radicals, i.e. the so-called homoallylic rearrangement, is rapid [15] and that naphthvalene is a typical aromatizable compound with a large strain energy (≈ 65 kcal/mol [16]) compared with that (27 kcal/mol [17]) of cyclopropane.









(1) In both benzene and ethanol, ${}^{1}NNV^{*} \rightarrow {}^{3}NNV^{*}$ intersystem crossing competes with ${}^{1}NNV^{*} \rightarrow NN$ valence isomerization, i.e. neither ${}^{1}NN^{*}$ nor ${}^{3}NN^{*}$ is formed upon excitation of NNV. (2) Although no reaction of ${}^{3}NNV^{*}$ is observed in benzene, ${}^{3}NNV^{*}$ in ethanol abstracts a hydrogen atom from the solvent molecule generating NNVK and 1-hydroxy-1-ethyl radical (R^{*}). (3) Interestingly, NNVK \rightarrow NNK valence isomerization is also rapid and recombination of two NNK thus formed yields naphthopinacol (NP) in accordance with the results obtained for NN in ethanol.

In spite of the generation of the ketyl radicals at room temperature, however, the decay rate constants of ³NNV^{*} and ³NN^{*} in ethanol are somewhat smaller than those in benzene. We thus suppose that the rates of hydrogen-atom abstraction by ³NNV^{*} and ³NN^{*} from ethanol are very slow compared with the ³NNV^{*} \rightarrow NNV and ³NN^{*} \rightarrow NN transition rates. In fact, as shown in Figs. 3 and 4, the absorption intensity of NNK^{*} is one order of magnitude smaller than those of ³NNV^{*} and ³NN^{*}, even if their absorption coefficients are different from that of NNK. Owing to a $\pi\pi^*$ or mixed $n\pi^* - \pi\pi^*$ character of ³NNV^{*} and ³NN^{*}, furthermore, their transitions to the ground states in benzene may be faster than those in ethanol.

Acknowledgements

This work was supported by a Grant-in-Aid for Priority-Area-Research on Photoreaction Dynamics from the Ministry of Education, Science, Sports and Culture of Japan (No. 06239101 and 06239106).

References

- [1] S. Miki, K. Matsuo, M. Yoshida and Z. Yoshida, Tetrahedron Lett. 29 (1988) 2211.
- [2] T. Nakayama, T. Yamaguchi, K. Ushida, K. Hamanoue, S. Miki, K. Matsuo and Z. Yoshida, Chem. Phys. Lett. 148 (1988) 259.
- [3] T. Nakayama, Y. Amijima, K. Ushida and K. Hamanoue, Chem. Phys. Lett. 258 (1996) 663.
- [4] S. Miki, H. Kagawa, K. Matsuo, O. Kobayashi, M. Yoshida and Z. Yoshida, Tetrahedron 48 (1992) 1567.
- [5] S. Miki, T. Ema, R. Shimizu, H. Nakatsuji and Z. Yoshida, Tetrahedron Lett. 33 (1992) 1619.
- [6] S. Miki, J. Ito, R. Noda, N. Nishijima and K. Fukunishi, Tetrahedron 52 (1996) 4269.

- [7] M.D. Newton, J.M. Schulman and M.M. Manus, J. Am. Chem. Soc. 96 (1974) 17.
- [8] N.J. Turro, P. Lechtken, A. Lyons, R.R. Hautala, E. Camahan and T.J. Katz, J. Am. Chem. Soc. 95 (1973) 2035.
- [9] T.J. Katz, E.J. Wang and N. Acton, J. Am. Chem. Soc. 93 (1971) 3782.
- [10] K. Ushida, T. Nakayama, T. Nakazawa, K. Hamanoue, T. Nagamura, A. Mugishima and S. Sakimukai, Rev. Sci. Instrum. 60 (1989) 617.
- [11] J.N. Pitts, R.L. Letsinger, R.P. Taylor, J.M. Patterson, G. Recktenwald and R.B. Martin, J. Am. Chem. Soc. 81 (1959) 1068.
- [12] R. Matsushima, T. Kishimoto and M. Suzuki, Chem. Lett. (1976) 579.
- [13] R. Nakashima, K. Okamoto and T. Matsuura, Bull. Chem. Soc. Jpn. 49 (1976) 3355.
- [14] T. Shimizu, Y. Torii, S. Miki, T. Nakayama and K. Hamanoue, Abstract of the Symposium on Photochemistry, Nagoya, Japan, 1996, p. 286.
- [15] J.K. Kochi, P.J. Krusic and D.R. Eaton, J. Am. Chem. Soc. 91 (1969) 1877.
- [16] N.C. Baird and M.J.S. Dewar, J. Am. Chem. Soc. 91 (1969) 352.
- [17] N.S. Isaacs, Physical organic chemistry (Longman, Harlow, 1987) p. 282.