An Intermediate for Naphthoylnaphthvalene → Naphthoylnaphthalene Valence Isomerization Originating from the Lowest Excited Singlet State

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By measurements of the absorption, phosphorescence and transient absorption spectra, the photoproduct obtained by steady-state photolysis of the title compound (NNV) at 77 K is tentatively ascribed to a zwitterionic intermediate for NNV→ naphthoylnaphthalene valence isomerization originating from the lowest excited singlet state.

The photochemistry of valene-type compounds is of great interest owing to the large strain energy and the peculiar sp^9 hybridization in the bicyclobutane moiety.[1] In connection with this, Turro et al.[2] 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. For naphthoylnaphthvalene (NNV) in benzene and ethanol at room temperature, however, we obtained the following results;[3] (1) intersystem crossing from the lowest excited singlet (^{1}NNV*) to triplet (^{3}NNV*) states competed with valence isomerization of ^{1}NNV* yielding ground-state naphthoylnaphthalene (NN); (2) the NNV ketyl radical (generated by hydrogen-atom abstraction of ^{3}NNV* from ethanol) also underwent rapid valence isomerization and recombination of two NN ketyl radicals thus formed yielded 1,1,2,2-tetranaphthyl-1,2-ethanediol. In order to find out the existence of an intermediate for ^{1}NNV*→NN valence isomerization, therefore, the present paper deals with the photochemistry of NNV at 77 K.

Details of the methods of preparation and purification of NNV and NN were given previously,[3] and the solvent used was a mixed solvent (EPA) of diethyl ether/isopentane/ethanol (5:5:2 in volume ratio). Although Uvasol diethyl ether (Merck) was 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 all experiments were performed at 77 K. Steady-state photolysis of NNV was carried out using the 313 nm monochromatic light selected from a USH-500D super-high-pressure mercury lamp. And then, for the photoproduct thus obtained, measurements of the absorption, phosphorescence and transient absorption spectra as well as the lifetimes of phosphorescence and transient absorption were performed: The absorption and phosphorescence spectra were obtained using a Hitachi 200-20 spectrophotometer and a Hitachi MPF-4 spectrophosphorimeter, respectively, and the transient absorption spectrum was recorded using the 355 nm excitation light pulse (with a full width at half-maximum intensity of 5 ns) from a Nd^{3+}:YAG laser (Continuum Surelight I) equipped with a multichannel analyzer;[4] the decay curves of phosphorescence and transient absorption were analyzed by means of a combination of a photomultiplier (Hamamatsu R329) with a storage oscilloscope (Iwatsu TS-8123).

Figure 1 shows the absorption spectral change caused by steady-state photolysis of NNV in EPA at 77 K (cf. the solid spectra). After photolysis, elevation of temperature up to room temperature followed by re-cooling to 77 K gives rise to the appearance of the dashed spectrum which is identical with the absorption spectrum of NN. This

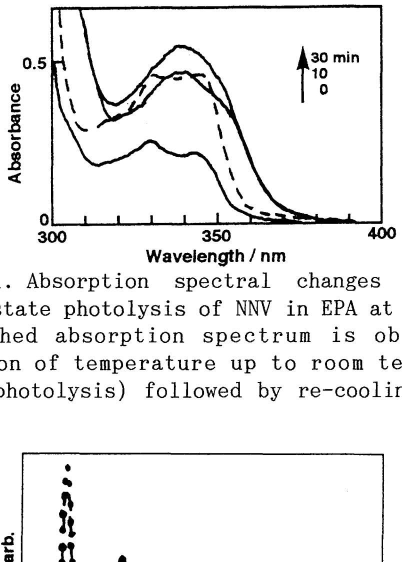


Figure 1. Absorption spectral changes caused by steady-state photolysis of NNV in EPA at 77 K (——). The dashed absorption spectrum is obtained by elevation of temperature up to room temperature (after photolysis) followed by re-cooling to 77 K.

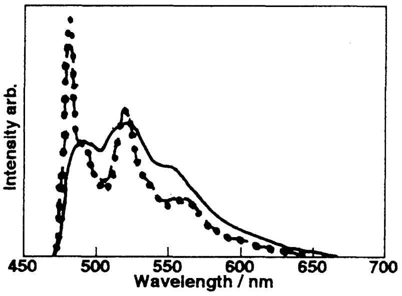


Figure 2. The phosphorescence spectrum (——) obtained for P-77 which is formed upon 30 min steady-state photolysis of NNV in EPA at 77 K. The dashed phosphoresce spectrum is obtained by elevation of temperature up to room temperature (after photolysis) followed by re-cooling to 77 K, and the dotted phosphorescence spectrum is obtained for NN.

indicates that the photoproduct (P-77) obtained at 77 K is different from NN which is formed at room temperature.^{3} In accordance with this, as shown in Figure 2, the phosphorescence spectrum (the solid line) obtained for P-77 is clearly different from that (the dotted line) obtained for NN and elevation of temperature up to room temperature (after photolysis) followed by re-cooling to 77 K changes the solid spectrum to the dashed spectrum. This dashed spectrum is identical with the phosphorescence spectrum obtained for NN and the phosphorescence excitation spectrum obtained for P-77 is confirmed to be identical with its absorption spectrum.

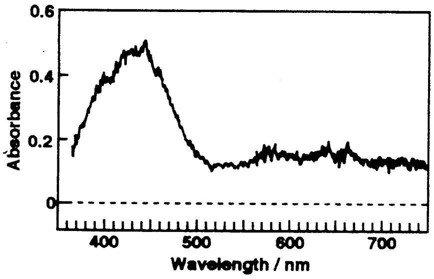
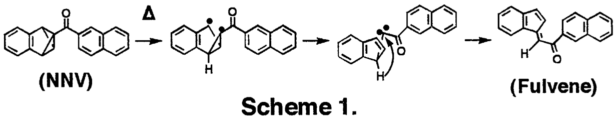


Figure 3. The transient absorption spectrum obtained by nanosecond laser photolysis of P-77 in EPA at 77 K.

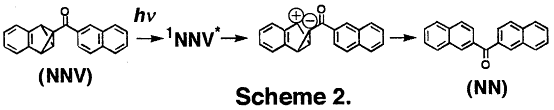
The transient absorption spectrum shown in Figure 3 is obtained by nanosecond laser photolysis of P-77 in EPA at 77 K and this spectrum can be assigned to the triplet-triplet absorption originating from the lowest excited triplet state of P-77. This is based on the following facts; (1) the lifetime (0.6-0.9 s) of transient absorption is equal to the corresponding phosphorescence lifetime; (2) in regard to the spectral profile and the lifetime, the transient absorption spectrum obtained for P-77 is somewhat different from those obtained for the lowest excited triplet states of NNV and NN with lifetimes of $\sim$1 s.^{3}

All the results stated above are similar to those obtained in methylcyclohexane, 3-methylpentane and 2-methyltetrahydrofuran. This indicates that P-77 is different from the NNV and NN ketyl radicals which are generated by hydrogen-atom abstraction of ^{3}NNV* from ethanol at room temperature.^{3} Hence, P-77 may be an intermediate for ^{1}NNV* →NN valence isomerization.

Many thermal reactions of the valene-type compounds are well known, and, for example, Turro et al.^{5} have observed quantitative formation of benzene from benzvalene. In contrast, Katz et al.^{6} have reported formation of benzofulvene and its polymer from naphthvalene, where no naphthalene is obtained and formation of benzofulvene can be interpreted in terms of the stepwise scission of C-C bonds in the bicyclobutane skeleton, i.e., generation of 2,3-benzobicyclo[3.1.0]hexen-4,6-diyl biradical and then indenyl carbene followed by migration of the benzylic hydrogen atom to the carbene center. This is based on the fact that bicyclo[3.1.0]hex-2-en-4,6-diyl biradical is postulated as an intermediate for benzene→fulvene valence isomerization by Bryce-Smith and Longuet-Higgins.^{7} Upon heating of NNV, we have also confirmed formation of a benzofulvene-type compound with a naphthoyl group at the exo-methylene carbon. This thermal reaction, therefore, can be understood by a mechanism shown by Scheme 1 which is essentially identical with that proposed for the thermal reaction of naphthvalene.



Scheme 1.



Scheme 2.

Since photolysis of NNV at room temperature yields ground-state NN, P-77 should be different from the biradical or the carbene shown in Scheme 1. We thus tentatively propose that P-77 is a zwitterionic species (cf. Scheme 2) and its observation at 77 K can be ascribed to the stabilization of positive and negative charges owing to their delocalization over the benzene ring and the naphthoyl group, respectively. Naturally, this conjecture is hardly speculative but the existence of such a zwitterionic species can be supported by the result obtained by Kaplan et al.^{8} who have also postulated a similar zwitterionic species as an intermediate for formation of 4-trifluoroethoxy-2-bicyclo[3.1.0]hex-2-ene upon photolysis of benzene in trifuluoroethanol at room temperature.

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