Photoinduced Intramolecular Proton Transfer and Intermolecular Hydrogen-Atom Abstraction of 1-Piperidinoantraquinone (PAQ)

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The lowest excited singlet and triplet states of PAQ give rise to formation of the N-ylide compound at 77 K and the reduced compound at room temperature, respectively. In the latter case, however, indirect population of the lowest excited triplet state from a higher excited singlet state (through a higher excited triplet state) is very important.

For photoinduced intramolecular hydrogen-atom transfer of 1-methylanthraquinone (MAQ)[1] and 1,4-dimethylanthraquinone (DMAQ),[2] we reported that both the lowest excited singlet (S_1) and triplet (T_1) states generated the corresponding excited biradicals followed by formation of the methides (9-hydroxy-1,10-anthraquinone-1-methide and 9-hydroxy-4-methyl-1,10-anthraquinone-1-methide, respectively); these methides were stable at 77 K but rapidly reverted to the original anthraquinones at room temperature. An interesting photochemistry of DMAQ in ethanol at room temperature was formation of 1,4-dimethyl-9,10-dihydroxyanthracene from not the T_1 state but the third excited singlet or triplet state. In accordance with photoreduction of anthraquinone and haloanthraquinones,[3,4] however, the T_1 state of MAQ gave rise to formation of 1-methyl-9,10-dihydroxyanthracene. In comparison with the absorption spectra of anthraquinones (with the S_1 states of typical $n\pi^*$ character) stated above, that of 1-piperidinoanthraquinone (PAQ) reveals the S_1 state to be of charge-transfer character. Hence, the present paper deals with intramolecular proton transfer and intermolecular hydrogen-atom abstraction originating from the S_1 and T_1 states of PAQ, respectively.

Following the method reported by Inoue et al.,[5] PAQ was synthesized from 1-chloroanthraquinone and piperidine; for purified PAQ, no genuine fluorescence and phosphorescence were observed. The solvents used were ethanol and EPA (diethyl ether/isopentane/ethanol=5:5:2 in volume ratio). Although diethyl ether (Uvasol, 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 steady-state photolysis was carried out using the 313-,405- or ≧510-nm light selected from a USH-500D super-high-pressure mercury lamp; the resulting absorption spectral change was recorded using a Hitachi 200-20 spectrophotometer. Nanosecond laser photolysis was performed using the third harmonic (the 355-nm light pulse with a full width at the half-maximum intensity of 5 ns) from a Nd^{3+}:YAG laser and the transient absorption spectra were recorded using a multichannel analyzer.[6]

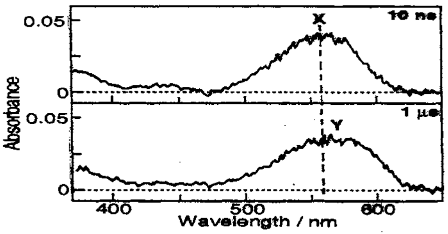


Figure 1. Transient absorption spectra obtained by nanosecond laser photolysis of PAQ in EPA at 77 K.

Figure 1 shows the transient absorption spectra obtained by nanosecond laser photolysis of PAQ in EPA at 77 K. Clearly, band X obtained at the end of pulse excitation (10 ns delay) is somewhat different from band Y (the residual absorption band) obtained at 1 μs delay; for band X, owing to the weak absorption and its small change with time, the decay curve can not be measured but the shift time of bands X to Y is estimated to be ~10 ns. As shown in Figure 2a, 313-nm steady-state photolysis of PAQ in EPA at 77 K causes the absorption spectral change which is found to be independent of the excitation wavelength, i.e., with the decrease of band R_2, band R_1 increases and two new bands ($P_{1,2}$) grow in: Since band Y shown in Figure 1 does not decrease with time, we believe that this band is

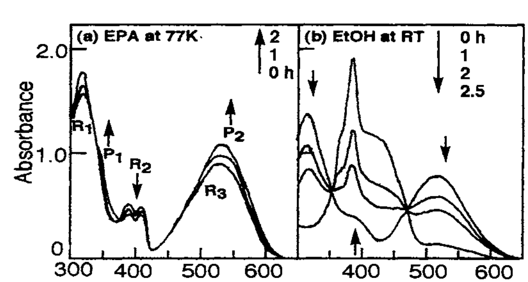
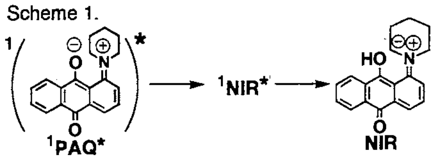


Figure 2. Absorption spectral changes upon steady-statephotolysis of PAQ in (a) EPA at 77 K and (b) ethanol at room temperature.

identical with band P_2 ; owing to the superposition of reactant and product absorptions, however, band P_2 looks like to be shifted to a shorter wavelength compared with band Y. After photolysis, the sample warming up to room temperature causes the disappearance of bands $P_{1,2}$ accompanied by the decrease and increase of bands R_1 and R_2, respectively. Since the absorption spectrum recorded after re-cooling of the sample down to 77 K is confirmed to be absolutely identical with that of PAQ in regard to the spectral profile and intensity, the photoproduct formed at 77 K may revert quantitatively to the original compound at a higher temperature than 77 K. This is consistent with no appearance of bands $P_{1,2}$ upon steady-state photolysis of PAQ at room temperature.

The spectral profiles of bands $P_{1,2}$ (observed at 77 K) and their disappearance accompanied by the appearance of absorptions due to only the original compound (upon elevation of temperature up to room temperature) are very similar to those observed for the absorption bands of several methides formed from alkylanthraquinones;[1,2,7] for MAQ[1] and DMAQ,[2] furthermore, picosecond and nanosecond laser photolysis revealed that both the S_1 and T_1 states underwent intramolecular hydrogen-atom transfer generating the corresponding excited biradicals followed by formation of the methides. By sub-picosecond laser photolysis of PAQ at room temperature,[8] generation of a transient species (responsible for band X) from the S_1 state (^{1}PAQ* with a lifetime of ~10 ps) can be seen; band Y can be observed clearly at 500 ps delay. However, no transient absorptions reflecting generation of an excited triplet species (or formation of the final product) from the T_1 state (^{3}PAQ*) can be seen; as shown in Figure 1, no such an evidence can also be obtained by nanosecond laser photolysis at 77 K. We believe that the final product responsible for band Y (identical with band P_2) is the N-ylide compound (NIR)[9] and thus band X can tentatively be ascribed to the absorption due to the lowest excited singlet state (^{1}NIR*) of NIR (cf. Scheme 1), i.e., ^{1}PAQ* of charge-transfer character undergoes intramolecular proton transfer (from the methylene group to the carbonyl oxygen) generating ^{1}NIR* followed by internal conversion to NIR. No observation of bands X and Y by nanosecond laser photolysis at room temperature may reflect rapid $^1\text{NIR*} \rightarrow \text{NIR} \rightarrow \text{PAQ}$ conversions; at 77 K, however, the former process may be somewhat suppressed and NIR can exist as the stable product.

Scheme 1.



A comparison of Figure 2a with Figure 2b indicates that 313-nm steady-state photolysis of PAQ in ethanol at room temperature causes the absorption spectral change different from that observed in EPA at 77 K. After photolysis at room temperature, furthermore, it is confirmed that introduction of air causes the quantitative conversion of the photoproduct back to the original compound. Since the product absorption band and its disappearance by introduction of air are very similar to those observed for 9,10-dihydroxyanthracenes formed by steady-state photolysis of anthraquinone and haloanthraquinones,[3,4] the photoproduct formed from PAQ at room temperature can safely be identified to be 1-piperidino-9,10-dihydroxyanthracene ($PAQH_2$). We thus conclude that ^{3}PAQ* abstracts a hydrogen atom from the solvent generating the semiquinone radical (PAQH•) followed by formation of $PAQH_2$. At room temperature, however, no absorptions due to ^{3}PAQ* and PAQH• can be seen by sub-picosecond and nanosecond laser photolyses, respectively. Furthermore, photoreduction of PAQ shown in Figure 2b is extremely slow compared with that of anthraquinone and haloanthraquinones.[3,4] These results may indicate that $^1\text{PAQ*} \rightarrow {}^3\text{PAQ*}$ intersystem crossing is very much slower than generation of ^{1}NIR* from ^{1}PAQ*. Since photoreduction of PAQ upon 405- or ≧510-nm excitation (initially populating the S_1 state) is found to be negligibly slow compared with that upon 313-nm excitation (initially populating a higher excited singlet state), intersystem crossing from a higher excited singlet state to a higher excited triplet state followed by internal conversion may be very important for population of the T_1 state, i.e., direct $S_1 \rightarrow T_1$ intersystem crossing is of minute importance for photoreduction of PAQ.

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