Photoinduced Intra- and Inter-Molecular Hydrogen-Atom Abstraction of 1-Methylanthraquinone

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The intramolecular hydrogen-atom abstraction in the lowest excited singlet and triplet states of 1-methylanthraquinone yields 9-hydroxy-1,10-anthraquinone-1-methide. The lowest excited triplet state at room temperature also abstracts a hydrogen atom from ethanol yielding 1-methyl-9,10-dihydroxyanthracene.

Both the lowest excited singlet and triplet states of 1,4-dimethylanthraquinone (DMAQ) cause the intramolecular hydrogen-atom abstraction yielding 9-hydroxy-4-methyl-1,10-anthraquinone-1-methide.[1] The intermolecular hydrogen-atom abstraction from ethanol yielding 1,4-dimethyl-9,10-dihydroxyanthracene is only observed upon excitation to the third excited singlet state. In contrast, 9,10-dihydroxyanthracene yielded from anthraquinone (AQ) is produced via its lowest excited triplet state.[2] We thus report the photoinduced intra- and inter-molecular hydrogen-atom abstraction of 1-methylanthraquinone (MAQ), since its photochemical behavior is expected to be similar to those of AQ and DMAQ.

MAQ was synthesized from phthalide and *o*-bromotoluene,[3] and the solvents used were ethanol and EPA (diethylether/isopentane/ethanol=5:5:2 in volume ratio). For the degassed sample solutions, nanosecond laser photolysis was performed using the second harmonic (347.2 nm) from a *Q*-switched ruby laser with a pulse duration of 20 ns.[4]

As shown in Fig. 1, the transient absorption spectra obtained by 347.2-nm nanosecond laser photolysis of MAQ in ethanol at room temperature have three absorption bands (B_1, B_2 and B_3). And, Fig. 2 indicates that the absorbance (A_t at 540 nm) of band B_1 (appeared within the duration of pulse excitation) further increases and then decreases to the zero absorbance following two single-exponential functions with rise and decay rate constants of k_R and k_{D_2}, respectively. In contrast, A_t (at 380 nm) of band B_3 (also appeared within a duration of pulse excitation) decreases to the zero absorbance following two single-exponential functions with decay rate constants of k_{D_1} and k_{D_2}; A_t (at 435 nm) of band B_2 decreases following a single-exponential function with a decay rate constant of k_{D_1}, and Fig. 1 reveals no existence of band B_2 at 1 μs delay. Upon 347.2-nm picosecond laser photolysis of MAQ in ethanol at room temperature, furthermore, the rate constant (k) for the single-exponential rise curve of band B_1 with time has been found to be $3.3\text{x}10^{10}$ s^{-1}.[5]

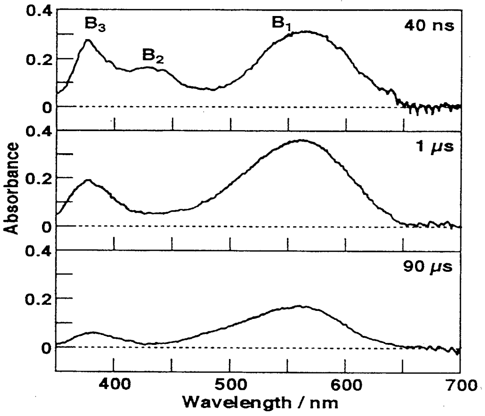


Figure 1. Transient absorption spectra obtained by 347.2-nm nanosecond laser photolysis of MAQ in ethanol at room temperature.

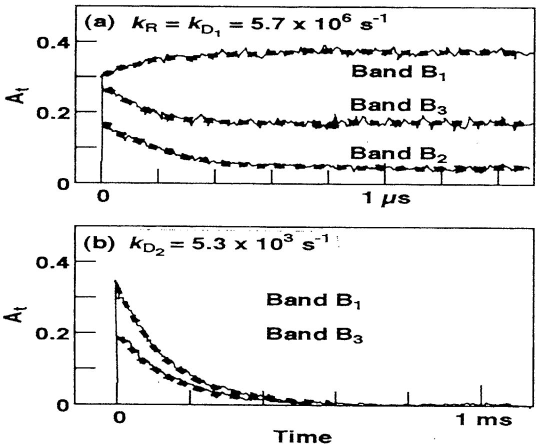
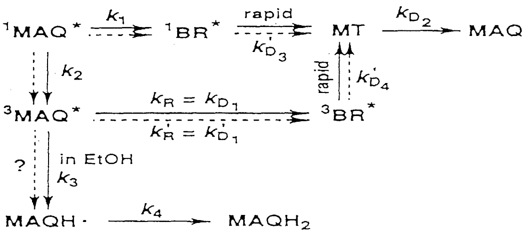


Figure 2. Changes in the absorbances (A_t) of bands B_1 (at 540 nm), B_2 (at 435 nm) and B_3 (at 380 nm) with time in ethanol at room temperature (solid curves). The dashed curves are best-fit single-exponential functions with rate constants (k_R, k_{D1} and k_{D_2}) indicated.

By 347.2-nm nanosecond laser photolysis of MAQ in EPA at 77K, similar transient absorption spectra are also obtained, but both bands B_1 and B_3 do not disappear completely even at a long delay time. Moreover, the absorbance changes of bands B_1, B_2 and B_3 with time reveal the existence of three transient species (with rise and decay rate constants of $k'_R=k'_{D1}=5.7\text{x}10^6$ s^{-1}, $k'_{D3}=4.9\text{x}10^4$ s^{-1} and $k'_{D4}=4.2\text{x}10^3$ s^{-1}) and one non-decay component. The absorption spectrum responsible for this non-decay component is very similar to that obtained by steady-state photolysis.

The transient absorption spectra obtained so far are similar to those of 9-hydroxy-1,10-anthraquinone-1-methides (MT) yielded from several alkylanthraquinones.[1,6] We thus conclude that both the lowest excited singlet (^{1}MAQ*) and triplet (^{3}MAQ*)



Scheme 1.

states of MAQ cause the intramolecular hydrogen-atom abstraction yielding the corresponding MT. Upon steady-state photolysis of MAQ at room temperature, no observation of the absorption spectrum responsible for a product yielded via MT reflects its rapid thermal reversion to MAQ.

The photochemistry of MAQ yielding MT at room temperature can be expressed by the processes shown by solid arrows in Scheme 1, that is; (1) ^{1}MAQ* yields both the excited singlet biradical (^{1}BR*, with a rate constant of k_1) and ^{3}MAQ* (with a rate constant of k_2), and a rate constant (k) obtained for the intensity increase of band B_1 in the picosecond time regime is the sum of k_1 and k_2, i.e., the ^{1}BR*→MT conversion is rapid; (2) band B_2 (and a decay component in band B_3) with a decay rate constant of k_{D1} is the triplet-triplet absorption due to ^{3}MAQ*, because the lowest excited triplet states of several anthraquinones have characteristic absorption bands at ~380-460 nm similar to bands B_2 and B_3;[7,8] (3) the slow rise component in band B_1 with a rate constant of k_R (=k_{D1}) thus reflects the formation of MT via the excited triplet biradical (^{3}BR*) generated from ^{3}MAQ*, i.e., the ^{3}BR*→MT process with spin conversion is rapid; (4) the complete disappearance of bands B_1 and B_3 with a rate constant of k_{D2}, reflects the thermal reversion of MT to MAQ. In EPA at 77 K, therefore, the rise and decay rate constants (k_R'= k_{D1}', k_{D3}' and k_{D4}') can be ascribed to the processes indicated by dashed arrows, i.e., the rapid formation of MT from both ^{1}BR* and ^{3}BR* at room temperature is suppressed and MT can exist as the stable product at 77 K.

Steady-state photolysis of MAQ in ethanol at room temperature yields 1-methyl-9,10-dihydroxyanthracene ($MAQH_2$) irrespective of the excitation wavelength. Undoubtedly, the intermediate for this photoreduction should be the semiquinone radical (MAQH) which is generated by intermolecular hydrogen-atom abstraction (from ethanol) of ^{3}MAQ*;[7] the disproportionation reaction between two MAQH$^\bullet$ yields $MAQH_2$ and MAQ simultaneously. Hence, Scheme 1 indicates that a decay rate constant obtained for the decay of ^{3}MAQ* (determined from the decay curves of band B_2 and B_3 shown in Fig. 2a should be equal to the sum of rate constants for the formation of ^{3}BR* (with a rate constant of k_{D1}) and MAQH$^\bullet$ (with a rate constant of k_3). Since the semiquinone radicals of several anthraquinones also have absorption bands around 380 nm,[7] the decay curve of band B_3 shown in Fig. 2b should be analyzed by a combination of first-order (with a rate constant of k_{D2}) and second-order (with a rate constant of k_4) reaction kinetics. In spite of these circumstances, all the decay curves of bands B_2 and B_3 can well be reproduced by first-order reaction kinetics with a rate constant of k_{D1} or k_{D2} which is equal to that determined from the rise (with a rate constant of k_R) or decay (with a rate constant of k_{D2}) curve of band B_1, respectively. For ^{3}MAQ*, we thus conclude that the rate of intramolecular hydrogen-atom abstraction from the methyl group is very rapid compared with that of intermolecular hydrogen-atom abstraction from ethanol. This is supported by the fact that the quantum yield (0.009) for the formation of $MAQH_2$ at room temperature is very small.

The mechanism for the formation of MT from MAQ is identical with that from DMAQ.[1] However, the lowest excited triplet state of MAQ also abstracts a hydrogen atom from ethanol generating MAQH$^\bullet$ which yields $MAQH_2$ as the final photoreduced product. In contrast, not the lowest excited triplet state but the third excited singlet state of DMAQ yields the corresponding photoreduced product. The formation of $MAQH_2$ via the lowest excited triplet state of MAQ can thus be ascribed to the existence of one carbonyl group not adjacent to the methyl group. In this sense, the photochemical behavior of the lowest excited triplet state of MAQ is dual, i.e., one is identical with that of AQ and the other is identical with that of DMAQ.

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