Photochemical reaction of [6]-1,4-cyclophaneanthraquinone

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Abstract. [6]-1,4-Cyclophaneanthraquinone (CHAQ) has been synthesized and its photochemical reaction is studied. Nanosecond laser photolysis of CHAQ in EPA at room temperature reveals that both the lowest excited singlet and triplet states of CHAQ cause the intramolecular hydrogen-atom abstraction yielding the 1,4-biradical, i.e., the hydrogen-atom abstraction by the carbonyl oxygen from the benzylic methylene of the cyclophane bridge. Since steady-state photolysis of CHAQ in EPA at 77 K reveals the formation of cyclophane-9-hydroxy-1,10-anthraquinone-1-methide (2), the results obtained by steady-state photolysis at room temperature are interpreted as follows: (1) In benzene, 2 changes to a naphthoquinone derivative (6). (2) In EPA, 2 yields its ethanol adduct (3) and there exists an equilibrium between 3 (major) and 6 (minor). (3) By a dark reaction, 3 and/or 6 revert very slowly to CHAQ.

Keywords. Cyclophaneanthraquinone; intramolecular hydrogen-atom abstraction.

1. Introduction

Pairs of isomeric molecules undergoing photochemical interconversion have been studied recently in an attempt to search for solar energy storage systems as well as molecular memory devices. We have thus been studying the photophysics and photochemistry of sterically strained polyacenequinone derivatives focusing on their photovalence isomerization (Nakayama *et al* 1988; Miki *et al* 1988, 1992b). Since [6]-1,4-cyclophaneanthraquinone (CHAQ) has a methylene bridge and one of the benzene rings is deformed to a boat form, it is expected that this compound can undergo photoisomerization yielding a hemi-Dewar type isomer. From these points of view, we have already prepared CHAQ and identified the final photoproduct to be cyclophane-hemi-Dewar-anthraquinone (Miki *et al* 1992c). Recently, however, we have found that this identification is incorrect owing to a low resolution of a ^1H NMR spectrometer (90 MHz). Hence, this review deals with results of our recent reinvestigation (Miki *et al* 1992a).

Although photochemistry of strain-free anthraquinones with a benzylic methylene has already been reported by Gritsan *et al* (1990, 1991), we believe that CHAQ is still an interesting compound because of its novel photochemical reaction which is different from that of several strain-free anthraquinones.

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2. Nanosecond laser photolysis of CHAQ in EPA (diethylether/isopentane/ethanol = 5:5:2 volume ratio) at room temperature

Starting from [6]-3,6-cyclophanephthalic acid prepared following the method by Liebe *et al* (1985), the title compound (CHAQ) is synthesized according to scheme 1; the final step is a modification of the method reported by Sammes and Dodsworth (1979).

Figure 1 shows the transient absorption spectra obtained by nanosecond laser photolysis of CHAQ in EPA at room temperature. In comparison with the spectrum obtained at the end of nanosecond pulse excitation (40 ns delay), those obtained at longer delay times have a weak absorption band at $\lambda_{\text{max}} = 385$ nm compared with that at $\lambda_{\text{max}} = 490$ nm. As shown in figure 2, the transient absorption monitored at 490 nm appears within the duration of the nanosecond pulse excitation (FWHM = 20 ns) and then grows further in following a single-exponential function with a rise time of 0.42 μs . In contrast, the transient absorption monitored at 385 nm decreases following a single-exponential function with lifetime equal to the rise time obtained for the 490-nm absorption. Hence, we have concluded that the transient absorption (with $\lambda_{\text{max}} = 490$ nm), which appeared within the duration of the nanosecond pulse excitation, is the absorption of the 1,4-biradical produced by the intramolecular hydrogen-atom abstraction at the lowest excited singlet of CHAQ and that the slow rise of the 490-nm absorption is due to the formation of the 1,4-biradical produced by the intramolecular hydrogen-atom abstraction at the lowest excited triplet state of CHAQ with an absorption maximum at 385 nm; the 1,4-biradical is produced by the hydrogen-atom abstraction of the carbonyl oxygen from the benzylic methylene.

Figure 1. Transient absorption spectra obtained by nanosecond laser photolysis of CHAQ in EPA at room temperature.

Figure 2. Single-exponential rise (at 490 nm) and decay (at 385 nm) of transient absorptions obtained by nanosecond laser photolysis of CHAQ in EPA at room temperature.

3. Steady-state photolysis of CHAQ in EPA at 77 K and at room temperature

Figure 3 shows the absorption spectral change caused by 405-nm steady-state photolysis of CHAQ in EPA at 77 K (cf. full lines). With the spectral decrement due to the reactant absorption, a new absorption band with $\lambda_{\text{max}} = 542$ nm as well as that at 300–400 nm grows in. One can clearly observe two isosbestic points at 476 and 406 nm. In comparison with the absorption spectra of 9-hydroxy-1,10-anthraquinone-1-methide and its derivatives as reported by Gritsan *et al* (1990, 1991), we propose that the product obtained at 77 K is cyclophane-9-hydroxy-1,10-anthraquinone-1-methide (2 in scheme 2) produced via the 1,4-biradical.

After steady-state photolysis at 77 K, the sample warming up to room temperature gives rise to the disappearance of the 542-nm band and the appearance of another new band at ~ 340 nm as well as that of the reactant (CHAQ) (cf. dotted line). After this, a 1-day dark reaction causes the spectral change from the dotted to the dashed spectra, indicating that a shoulder at longer wavelengths decreases with accompanying increase of the absorption due to the reactant (CHAQ). These results indicate that

Changing the solvent from EPA to $^{[2]H}$ chloroform *in vacuo*, analysis of the photoproducts has been performed using a 1H NMR spectrometer (300 MHz). Although the NMR signals obtained are very complicated, the formation of **3** (cf. scheme 2) as the main product is really confirmed; 8.55 ppm (s, 2H, OH) and 5.97 ppm (s, 2H, olefin); 3.94 ppm (*dq*, 2H) and 3.51 ppm (*dq*, 2H) for the diastereotopic methylene

Figure 4. Spectral change caused by 405-nm steady-state photolysis of CHAQ in EPA at room temperature (full lines). By a 2-day dark reaction after photolysis, the dashed spectrum is obtained.

protons of the ethoxy groups. We thus suppose that **3** is formed from **2** following the mechanism shown by scheme 2. Since the highly strained enone part of **2** is expected to be very reactive, addition of ethanol to this compound may give rise to the formation of **4**, releasing the strain of the exomethylene group followed by the 1,5-hydrogen-atom shift finally yielding **5**. After this, addition of ethanol to **5** may produce strain-free **3**. Based on the well-known fact that anthrahydroquinone and its derivatives are fluorescent, we have assigned the dashed spectrum shown in figure 2 or 3 to the absorption of **3** because its fluorescence excitation spectrum is identical with the absorption spectra shown by the dashed lines in figures 2 and 3.

On keeping the sample solution in the dark for a long time, the NMR signals due to **3** disappear with the accompanying appearance of not only the signals due to ethanol but also those due to recovered CHAQ. This thermal reversion may be interpreted in terms of ethanol elimination from **3**.

4. Steady-state photolysis of CHAQ in benzene at room temperature

As shown in figure 5, 405-nm steady-state photolysis of CHAQ in benzene at room temperature reveals the spectral change somewhat different in form from that obtained in EPA at room temperature (cf. figure 4). After photolysis, a 1-day dark reaction causes spectral decrement and increment due to the product and the reactant, respectively (cf. dashed line). In [$^2\text{H}_6$] benzene, photolysis of CHAQ is also performed and then the results of ^1H NMR analysis obtained are as follows: 6.51 ppm (*d*, 1H, $J = 9.9$ Hz), 5.50 ppm (*d*, 1H, $J = 9.9$ Hz) and 5.03 ppm (*dd*, 1H, $J = 5.4$ and 11.7 Hz). Although product identification based on the NMR signals alone is not satisfactory enough, we believe that at least a methylene cyclohexene moiety really exists. We thus tentatively propose that **6** is produced via **2**.

Since similar NMR signals are observed even in EPA, **6** in this solvent may be a minor product. This is supported by the following facts: (1) The dotted spectrum shown in figure 2 can be interpreted in terms of the superposition of the absorption due to **3** on that due to **6**. (2) The photochemistry of CHAQ at room temperature in EPA is found to be identical to that in ethanol. After photolysis in ethanol, we thus have changed the solvent to benzene and found that the absorption spectrum of **3** changes very slowly to that of **6** and reverted CHAQ.

Figure 5. Spectral change caused by 405-nm steady-state photolysis of CHAQ in benzene at room temperature (full lines). By a 1-day dark reaction after photolysis, the dashed spectrum is obtained.

5. Conclusions

Although [6]-1,4-cyclophaneanthraquinone (CHAQ) is a sterically strained compound, the photoinduced intramolecular hydrogen-atom abstraction is identical with that of several strain-free anthraquinones with a benzylic methylene (Gritsan *et al* 1990, 1991). In the latter cases, however, 9-hydroxy-1,10-anthraquinone-1-methides produced via the 1,4-biradicals easily revert to the original anthraquinones. In this sense, we believe that the photochemistry of CHAQ presented here is very unique and interesting.

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