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Photochemical Addition Reactions of Methanol and Ethanol to 1,4-Diaminoanthraquinone

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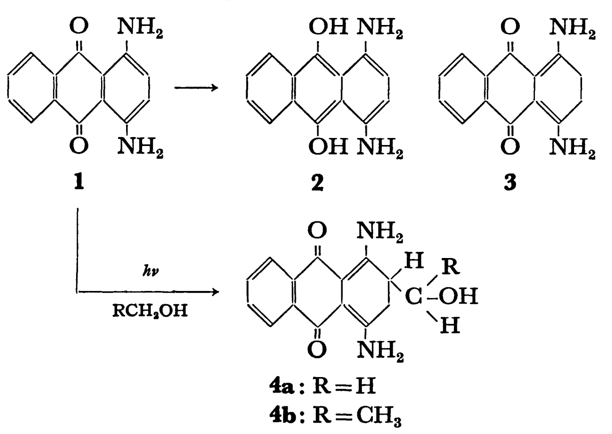
Synopsis. Photochemical reactions of 1,4-diaminoanthraquinone in methanol and/or ethanol yielded solvent adducts, **4a** and **4b**. The reactions proceeded *via* an upper triplet state. The quantum yields were 0.013—0.019 at 280 nm.

Anthraquinone compounds undergo various photochemical reactions.[1] The photoreductions have been the most extensively studied. 9,10-Anthracenediol is, as is well known, formed on the irradiation of anthraquinone in a reducing solvent.[2]



1 **2** **3**

hν RCH₂OH

4a: R=H
4b: R=CH$_3$

Several works have been undertaken on the photofading reactions of 1,4-diaminoanthraquinone (**1**) and its homologues because of their industrial importance as dyestuffs. A 9,10-anthracenediol compound (**2**) or its leuco-tautomer (**3**) has been proposed as a product, by analogy with anthraquinone.[3] In the present investigation, however, we observed solvent addition reactions; that is, compounds **4a** and **4b** were obtained on the irradiation of **1** in methanol and ethanol respectively. Similar photoinduced solvent additions have been reported for unsaturated ketones,[4] lactones,[5] and acridines.[6]

Results and Discussion

The irradiation of air-free solutions of **1** yielded the solvent adducts, **4a** and **4b**. The adducts were isolated by preparative thin-layer chromatography (TLC) in 30—40% yields. Neither **2** nor **3** was detected in the reaction mixture.

The wavelength effects on the reaction were investigated by irradiation with monochromatic lights of various wavelengths. No substantial reaction was observed for the light at visible-region band which is assigned to the charge-transfer (CT) transition associated with the charge migration from the amino group to the carbonyl group.[7] The light shorter than 300 nm gave rise to the degradation of **1**. It should be noted that the sunlight still has enough intensity in this wavelength region to cause troublesome photofading of dyed fabrics. The quantum yields for the disappearance of **1** were below 0.02 and reached their maxima around 280 nm, as is shown in Fig. 1. According to Inoue *et al.*, the band at 280 nm is ππ* in nature and is polarized along the axis parallel to the C=O bond.[7]

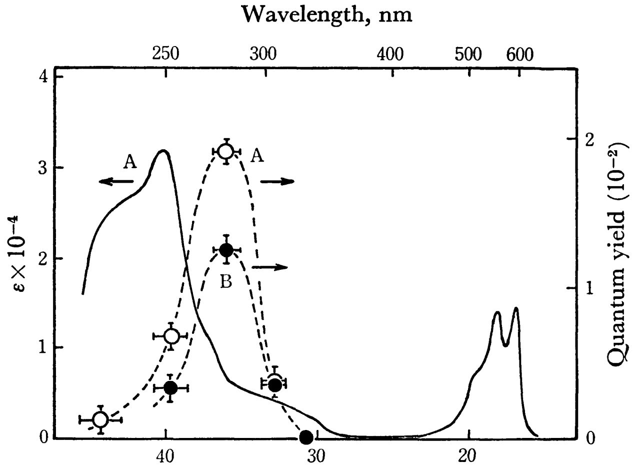


Fig. 1. Electronic spectrum of **1** and quantum yields for its disappearance. A: Ethanol solution; B: methanol solution.

The reaction undoubtedly proceeded *via* a triplet state, as is indicated by the fact that the photo-addition was sensitized by acetophenone and benzophenone[8] and quenched by piperylene. Neither phenanthrene nor biacetyl sensitized the reaction. Hence, the triplet energy for the reaction was estimated to be 62—68 kcal/mol.[9] This is close to the anthracene triplet energy of 62.7 kcal/mol.[10]

Davies *et al.* distinguished between the photoreduction in alcoholic solutions of "strong" sensitizers, such as, for example, anthraquinonesulfonates, and "weak" sensitizers, such as aminoanthraquinone.[11] The former have the lowest triplet of the nπ* type, which abstracts hydrogen efficiently from the substrates to initiate the reaction. On the other hand, the CT triplet lies below the nπ* triplet in the weak sensitizer. The CT state of **1** does not cause any significant reaction. Evidently the reaction is associated with the upper triplet. The participation of an upper triplet was also pointed out in the photoreduction of 1-dimethylaminoanthraquinone.[12] There still remains a question which character, nπ* or ππ*, the triplet has in the present reaction.

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Radical-chain processes have been proposed for the photoinduced solvent-addition reactions of 2-cyclopentenone[4c)] and α,β-unsaturated lactones[5)] from the facts that the quantum yields exceeded unity[4c,5)] and that the same adducts could be obtained in the thermal radical reactions.[5)] It might seem that the low quantum yields in the present photoreactions do not afford positive support to the radical-chain mechanism. However, **4b** can be prepared by decomposing azobis(isobutyronitrile) in the ethanol solution of **1**. It can, thus, be presumed that the quantum yield for the solvent addition remains far below unity even if the mechanism involves a radical-chain processes, because **1** gives so low a quantum yield for the triplet formation,[10)] and the active triplet might decay rapidly through a subsequent internal conversion to the inactive CT triplet, leaving a really small quantum yield to initiate the radical process. One cannot overlook other possibilities as well, such as a radical cage reaction or nonradical processes.

Experimental

The IR spectra were obtained on a Hitachi-Perkin-Elmer Model 125 spectrophotometer. The UV spectra were taken on a Shimadzu UV-200 or a Hitachi 101 spectrometer. The proton NMR spectra were recorded with a Hitachi R-24 spectrometer at 60 MHz, using tetramethylsilane as the internal standard.

Materials. Compounds **1** and **3** were supplied by the Nihon Kayaku Co., Ltd., and were purified by recrystallization. All the other compounds were commercially available and were recrystallized before use. The methanol and ethanol were purified by the usual methods.

Photochemical Reaction. Solutions of 100 mg of **1** in 400 ml of alcohols were irradiated under nitrogen for 10 h at room temperature using an internal 100 W high pressure mercury lamp. The reaction period could be reduced to one-tenth by sensitizing the solution with 150 mg of benzophenone, while employing Pyrex as a filter. Each reaction mixture contained one main fluorescing product, along with unreacted starting meterials and traces of unidentified by-products, as revealed by silica gel TLC with a benzene–ethyl acetate–methanol mixture (5: 5: 1) as the eluent. The R_f values were in this order: **4a**<**4b**<**3**. The adducts were isolated by preparative TLC as yellow powders in 30—40% yields. The low yields are mainly attributable to the poor recovery by the isolation. The products decomposed above 150 °C without showing definite melting points. They gave UV spectra which quite resembled that of **3**. Their structures were determined from the following data.

1,4-Diamino-2-hydroxymethyl-2,3-dihydroanthraquinone (**4a**): IR (KBr) 2925 (ν_{CH}, alkyl), 1610 ($\nu_{\mathrm{C=O}}$) and 1055 cm^{-1} ($\nu_{\mathrm{C-O}}$); NMR (CF$_3$CO$_2$H) τ 1.1—1.6 (m; C^5-H and C^8-H), 1.6—2.0 (m; C^6-H and C^7-H), 5.4—5.8 (m; methylene of CH$_2$OH) and 5.8—6.5 (m; C^2-H and C^3-H). Found: C, 58.57; H, 5.30; N, 8.85%. Calcd for $C_{15}H_{14}N_2O_3 \cdot 2H_2O$: C, 58.82; H, 5.88; N, 9.12%.

1,4-Diamino-2-(α-hydroxyethyl)-2,3-dihydroanthraquinone (**4b**): IR (KBr) 2970 (ν_{CH}, alkyl), 1612 ($\nu_{\mathrm{C=O}}$) and 1110 cm^{-1} ($\nu_{\mathrm{C-O}}$); NMR (CF$_3$CO$_2$H) τ 1.1—1.5 (m; C^5-H and C^8-H), 1.5—2.0 (m; C^6-H and C^7-H) 5.2—5.8 (m; methyne of CHOHCH$_3$), 6.1—6.5 (m; C^2-H and C^3-H) and 8.37 (d, J=6.0 Hz; methyl). In a pyridine solution the methyl signal splits into a pair of doublets, situated at τ 8.5 (J=6.0 Hz) and 8.6 (J=6.0 Hz). The splitting is considered to arise because the photoadduct is a mixture of the diastereomers. The separation of the diastereomers was attempted using TLC, but it was unsuccessful. Found: C, 60.28; H, 5.27; N, 8.98%. Calcd for $C_{16}H_{16}N_2O_3 \cdot 2H_2O$: C, 60.00; H, 6.25; N, 8.75%.

The isolated adducts were both relatively stable to air under room conditions, but they gradually oxidized on the TLC plate when exposed to air. UV, IR, and NMR analyses suggested the formation of 2-hydroxymethyl- and 2-(α-hydroxyethyl)-1,4-diaminoanthraquinone.

Quantum Yield. Degassed solutions of 2×10^{-5} mol/l in 1 cm quartz cells were irradiated at 25 ± 1 °C with monochromatic lights of various wavelengths, using a Nihon Bunko CRM-FA Spectral Irradiator equipped with a 2-kW xenon lamp and a 105 Integrator to monitor the light quanta irradiated. Potassium tris(oxalato)ferrate(III) actinometry was employed to calibrate the integrator at each selected wavelength. The light quanta transmitted by the reaction cells were also measured with other potassium tris(oxalato)ferrate(III) actinometer placed immediately behind the cells.

Thermal Radical Reaction. A solution of 10 mg of **1** and 200 mg of azobis(isobutyronitrile) in 100 ml of ethanol was kept at 64 °C for 5 h under nitrogen. After a work-up, the TLC analysis of the reaction mixture revealed the presence of **4b**, along with recovered **1**. The IR spectrum of the isolated product was identical with that of the photochemically obtained one.

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