BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (2), 351—354 (1979)

The Photochemical Reaction of Benzo[*c*]cinnoline. II. Photo-reduction in Acidic 2-Propanol

Hiroyasu Inoue,* Yukimi Hiroshima, and Norio Makita

Department of Applied Chemistry, Faculty of Technology, Kanagawa University, Kanagawa-ku, Yokohama 221

(Received July 22, 1978)

The photochemical reduction of benzo[*c*]cinnoline in strongly acidic 2-propanol (4 M HCl) has been studied using light of wavelength longer than 400 nm. The photoproduct has been identified as 5,6-dihydrobenzo[*c*]cinnoline. The quantum yields for product formation, which are the same as that for the disappearance of the reactant, have been measured under various conditions. In contrast to the poor phosphorescent property of benzo[*c*]cinnoline, the protonated species has been found to phosphoresce with significant efficiency. The lowest triplet state energy has been estimated to be 51 kcal/mol. The results of the quenching showed that the photoreduction was attributed to the lowest excited triplet state of protonated benzo[*c*]cinnoline. The pK_a value in the reactive state is lower than that in the ground state.

Several nitrogen heterocyclic compounds in electronically excited states have been shown to undergo hydrogen atom abstraction from solvent molecules. The photo-reductions of acridine and phenazine, for example, have been extensively studied, and the reactive states in the photo-reduction shown to be the lowest excited $n\pi^*$ singlet states.[1,2] The photo-reduction of phenazine has also been studied in acidic media, and the $n\pi^*$ singlet state mechanism proposed.[3] For quinoline and pyrimidine derivatives in acidic alcohol solutions, however, photoalkylation has been observed.[4,5]

In a previous paper[6] it was reported that the photoirradiation of benzo[*c*]cinnoline in strongly acidic (4M HCl) alcoholic solution led to the formation of 2,2′-diaminobiphenyl or carbazole as the final product depending on the excitation wavelength and the alcohol used as the solvent. In both reactions the final products are formed by the subsequent reactions of the initially formed intermediate which is characterized by absorption bands at 240, 270, and 316 nm. In the case of benzo[*c*]cinnoline in acidic 2-propanol, irradiation with light of a wavelength longer than 400 nm gives the intermediate compound, but no subsequent reaction occurs.[7]

In this paper, the initial photoreaction of benzo[*c*]cinnoline under certain conditions will be reported. Although some results indicate that the photoproduct is 5,6-dihydrobenzo[*c*]cinnoline, further evidence will be given for the identification of the product. This will be followed by a discussion of the reactive state of the reactant on the basis of the quantum yields for the reaction under various conditions.

Experimental

Materials. Benzo[*c*]cinnoline was obtained from Aldrich Chemical Co. and recrystallized from ethanol; mp 155 °C (lit,[8] 156 °C). 2-Propanol, a Kokusan Works reagent, was purified by refluxing in sodium hydroxide solution and subsequent distillation. Purified 2-propanol was shown to be free from aldehydes by GLC analysis.[9] Anthracene, pyrene, fluoranthene, *trans*-1,3-pentadiene, and naphthalene, which were used in quenching experiments, were purified by recrystallization or distillation.

Light Source and Irradiation. A 500 W high pressure mercury arc lamp (Ushio USH-500) was used as the visible light source with a Corning glass filter (CS3-73) which cut off light shorter than 400 nm. All irradiations were carried out at room temperature. The solution of the reactant was flushed with nitrogen passed through a pyrogallol solution for 30 min prior to and during the irradiation. Acidities of the solution were adjusted with HCl.

Actinometry and Analysis. The intensities of light transmitted by the sample solution and solvent respectively were measured to determine the quantum yields of the photoreaction using a potassium ferrioxalate solution as actinometer.[10] Two cylindrical cells (diameter: 4.5 cm, length: 3 cm) were used in the actinometry. The disappearance of benzo[*c*]cinnoline and the appearance of the product were determined spectrophotometrically. The molar extinction coefficients of the ultraviolet absorption bands of the photoproduct have been determined previously.[6]

Measurements. Ultraviolet absorption spectra were taken with a Shimadzu UV-200 spectrophotometer using 1 cm quartz cells. Emission spectra were recorded on a Shimadzu RF-500 spectrofluorimeter.

Chemical Reduction of Benzo[c]*cinnoline with Lithium Aluminium Hydride.* Benzo[*c*]cinnoline was chemically reduced by a large excess of lithium aluminium hydride in tetrahydrofuran under nitrogen at room temperature. After 30 min the solution was acidified by the addition of HCl and the absorption spectrum of the reduced compound was measured.

Results and Discussion

Photoproduct in Acidic Aqueous 2-Propanol. Figure 1 shows the spectral change caused by irradiation of the reactant (6.7×10^{-5} M) in acidic (4 M HCl) aqueous 2-propanol. The photo-reaction was completed in 140 min giving rise to a photoproduct having bands at 240, 270, and 316 nm. The existence of three isosbestic points at 235, 270, and 324 nm and the quantitative recovery of benzo[*c*]cinnoline by aeration of the irradiated solution indicate the absence of a side reaction.

In order to identify the product as 5,6-dihydrobenzo[*c*]cinnoline (monoprotonated form in strongly acidic solution), the chemical hydrogenation of the reactant was attempted. The hydrogenation was performed by treating the tetrahydrofuran solution of benzo[*c*]cinnoline with lithium aluminium hydride. The solution of the resulting reduced compound was acidified and the absorption spectrum determined. The observed spectrum is presented in Fig. 2. The chemically reduced compound has been considered to be 5,6-dihydrobenzo-

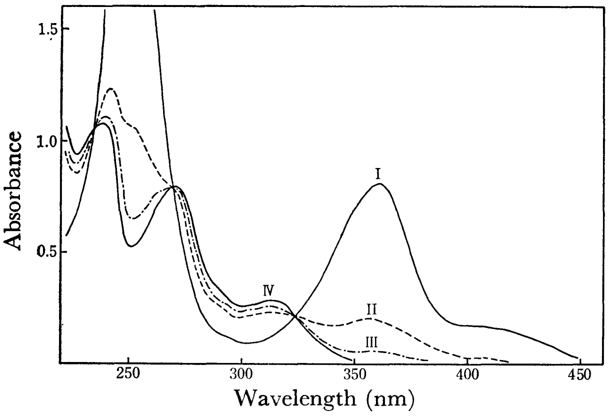

Fig. 1. Spectral change of the 4 M HCl 2-propanol solution of benzo[*c*]cinnoline (6.7×10^{-5} M) caused by irradiation with light longer than 400 nm. Irradiation time (min); I: 0, II: 30, III: 60, IV: 140.

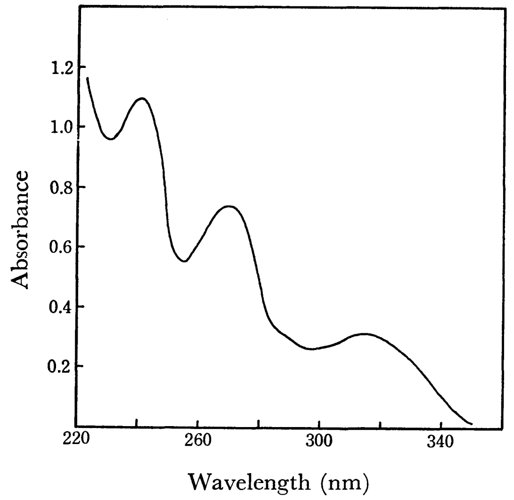

Fig. 2. Absorption spectrum of the acidified tetrahydrofuran solution of the compound prepared by reduction of benzo[*c*]cinnoline with $LiAlH_4$.

[*c*]cinnoline. As seen from Figs. 1 and 2, the absorption spectra of the products formed by the two methods show good agreement. Consequently, the photoproduct has been identified as 5,6-dihydrobenzo[*c*]cinnoline.

Quantum Yields for the Photo-reduction under Various Conditions. The quantum yield for the disappearance of the reactant coincides with that for product formation, thus indicating that 5,6-dihydrobenzo[*c*]cinnoline is the only photoproduct from the reactant in the present experimental conditions. As seen from Fig. 3, the quantum yield remained constant with variation in the irradiation time (15—120 min) and in the initial concentration of the reactant (4.0×10^{-5}—5.2×10^{-4} M). The average quantum yield has been determined to be 5.5×10^{-3}. For the photo-reduction of phenazine in alcoholic solution, the concentration dependence of the quantum yield has been established and interpreted in terms of self quenching.11) However, the result shown in Fig. 3b indicates that such self-quenching is absent in the present photo-reduction in the concentration range studied here.

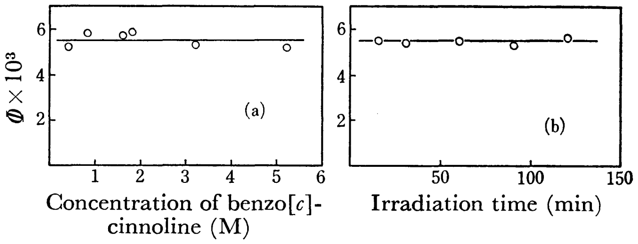

Fig. 3. Dependence of quantum yields for the photoreduction: (a) on the initial concentration of the reactant; (b) on irradiation time.

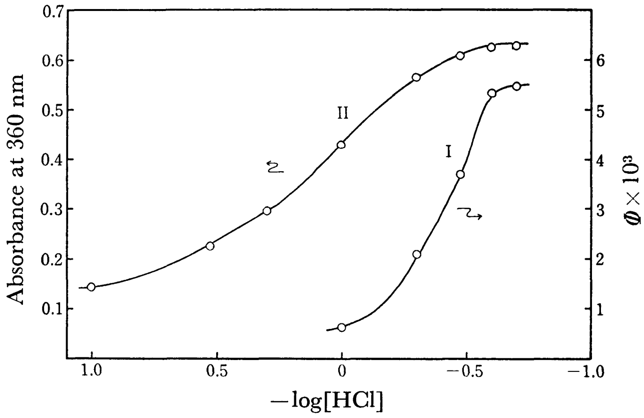

Fig. 4. Quantum yields for the photoreduction (I) and absorption intensity of the 360 nm band (II) at various concentrations of HCl.

It has been found that the quantum yield changes with variation in the acidity of the solution. Curve I in Fig. 4 shows the quantum yield at various concentrations of hydrochloric acid. In Fig. 4 the absorbances of protonated benzo[*c*]cinnoline at 360 nm have also been plotted against the acid concentration (curve II). From this curve the apparent pK_a of the conjugate acid of benzo[*c*]cinnoline in the ground state has been determined to be 0.1 in a mixed solvent of 2-propanol and water (1: 1) at 20 °C. Since only the protonated species of the reactant can be excited with visible light, curve I may be regarded as reflecting the equilibrium situation of the protonation at the reactive state in the photoreduction. From curve I the pK_a at the reactive state, which can be assigned as the lowest triplet state as described below, has been estimated to be −0.4. Therefore, the basicity of the reactant in the lowest triplet state is considered to be lower than that in the ground state and this behavior is in contrast to that for other nitrogen heterocyclic compounds which have higher pK_a values in the lowest triplet states than in the ground states.12–14)

Since hydrochloric acid was used to acidify the solution the quenching effect of chloride ion needs to be examined in view of the fact that in some cases halide ions act as fluorescence quenchers15) and exibit a quenching effect as in the photo-reduction of acridine.16) In the present case, the quantum yield has been found to be unaffected on addition of sodium chloride in the concentration range up to 0.05 M.

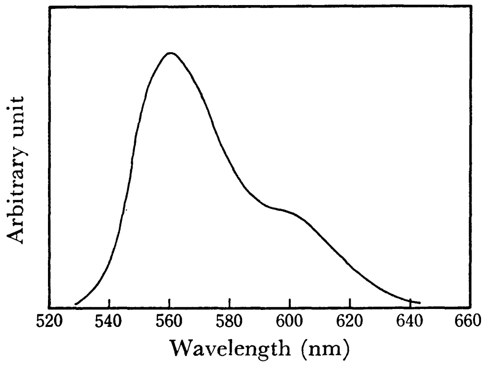

Fig. 5. Phosphorescence spectrum of protonated benzo-[*c*]cinnoline in 4 M HCl aqueous 2-propanol at 77 K. Excitation wavelength 420 nm.

Therefore, it is not necessary to correct the results concerning the effect of acid concentration on the quantum yield presented in Fig. 4 for changes in chloride ion concentration.

Emission Spectra of Protonated Benzo[c]*cinnoline.* It has been established that benzo[*c*]cinnloine exibits fluorescence, but does not phosphorescence with a significant quantum yield.[17] The lowest triplet state has been assigned as of the $\pi\pi^*$ type and the energy determined to be 52.0 kcal/mol from the $S_0 \rightarrow T_1$ absorption spectrum.[18] On the other hand, little is known concerning the excited states of the protonated species. In order to study the behavior of protonated benzo[*c*]cinnoline in electronically excited states, the emission spectra have been measured. In contrast to the non-phosphorescent property of the unprotonated species, the phosphorescence emission could be observed for the protonated species by means of a conventional spectrofluorimeter at 77 K, the observed phosphorescence band is shown in Fig. 5. On the other hand, the intensity of the fluorescence band at 490 nm decreased with increasing acid concentration. Since the phosphorescence band has no fine structure, the position of the 0-0 transition can not be determined precisely. Nevertheless, the wavelength of the peak (560 nm) may indicate the approximate energy of the lowest triplet state (E_T), that is, E_T has been estimated to be 51 kcal/mol. Recently, Lin *et al.*[19] have observed the enhanced phosphorescence band in isopentane solution containing fluorinated alcohols which can form hydrogen bonds with benzo[*c*]-cinnoline. The spectra have fine structure and the shortest wavelength peaks are at approximately 550 nm.

Quenching in the Photo-reduction. In order to investigate the reactive state of the reactant in the photoreduction, quenching experiments were conducted. Quenching during the photo-reduction has been studied quantitatively through measurements of the quantum yields. In consideration of the estimated value of the lowest triplet state of the reactant (E_T=51 kcal/mol), the following compounds have been employed in the quenching experiments, naphthalene (E_T=60.9 kcal/mol), *trans*-1,3-pentadiene (E_T=59.2 kcal/mol), fluoranthene (E_T=52.9 kcal/mol), pyrene (E_T=48.2 kcal/mol), and anthracene (E_T=42.7 kcal/mol).[20] Under the present experimental conditions, none of these compounds can absorb the irradiated light.

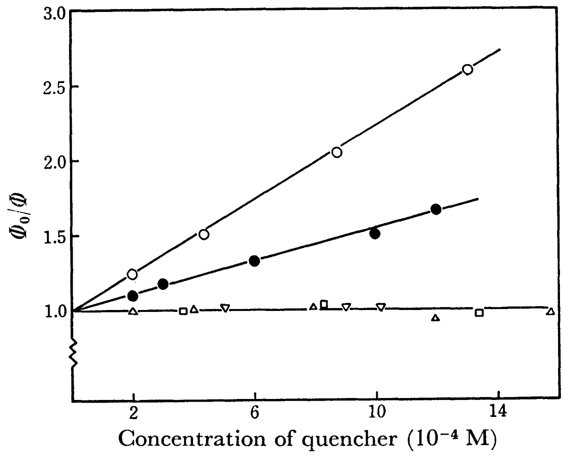

Fig. 6. Stern-Volmer plots for the photoreduction. ○: Anthracence, ●: pyrene, ▽: fluoranthene, △: *trans*-1,3-pentadiene, □: naphthalene.

The quenching experiments were performed using a fixed concentration of the reactant and variations in the quencher concentration. The quenching data are presented in Fig. 6, where Φ_0/Φ have been plotted against the quencher concentrations. The quantities Φ and Φ_0 are the quantum yields with and without quencher, respectively. As can be seen from Fig. 6, pyrene and anthracene act effectively as quenchers for the photo-reduction and the Stern-Volmer plots give straight lines, thus indicating that a single excited state participates in the photo-reduction. Fluoranthene, *trans*-1,3-pentadiene, and naphthalene exibited no influence on the quantum yield. Taking into account the lowest triplet state energies of the reactant and the quenchers, the triplet-triplet energy transfers from the protonated benzo[*c*]cinnoline donor to the pyrene and anthracene acceptors are considered possible, whereas such energy transfer are impossible in other cases. These situations reflect the results obtained here. Therefore, the observed quenching effects have been interpreted in terms of the triplet-triplet energy transfer. This is also indicated by the phosphorescence quenching data as shown in Fig. 7, where I_0/I has been plotted against the concentration of pyrene acceptor. The quantities I and I_0 are phosphorescence intensities at 560 nm with and

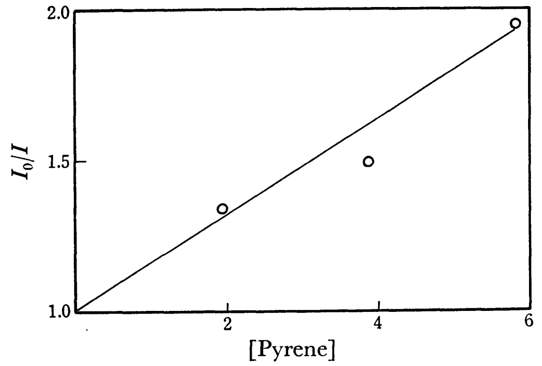

Fig. 7. Phosphorescence quenching plots of protonated benzo[*c*]cinnoline by the pyrene acceptor.
Excitation wavelength: 362 nm. Concentration of benzo[*c*]cinnoline: 1.04×10^{-4} M.

without pyrene. It is evident that pyrene acts as a triplet quencher.

The lowest excited singlet state energy of the protonated benzo[*c*]cinnoline has been estimated to be 68 kcal/mol from the longest wavelength absorption band at 420 nm. This value is lower than that of any compound used in the quenching experiments,[20] and therefore, the singlet-singlet energy transfer may be dismissed as responsible for the observed quenching. From the absorption and emission spectra, no evidence was obtained for the ground state complexing and the exciplex formation between the reactant and the quenchers.

Consequently, the results suggest that the reactive state in the photo-reduction in strongly acidic aqueous 2-propanol is the lowest excited triplet state of protonated benzo[*c*]cinnoline.

References

1) D. G. Whitten and Y. J. Lee, *J. Am. Chem. Soc.*, **93**, 961 (1971).

2) G. A. Davis, J. D. Gresser, and P. A. Carapellucci, *J. Am. Chem. Soc.*, **93**, 2179 (1971).

3) D. N. Bailey, D. K. Roe, and D. M. Hercules, *J. Am. Chem. Soc.*, **90**, 6291 (1968).

4) F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Am. Chem. Soc.*, **92**, 2745 (1970).

5) M. Ochiai, E. Mizuta, Y. Asahi, and K. Morota, *Tetrahedron*, **24**, 5861 (1968).

6) Part I of this series: H. Inoue, T. Sakurai, and F. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 924 (1975).

7) The photoproduct has no absorption at wavelength longer than 400 nm.

8) G. M. Badger, J. H. Seidler, and B. Thomson, *J. Chem. Soc.*, **1951**, 3207.

9) If 2-propanol is contaminated with aldehydes, the initial photo-reduction is followed by the subsequent reaction to give 2,2′-diaminobiphenyl to be published.

10) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

11) T. Iwaoka, S. Niizuma, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **43**, 2786 (1970).

12) G. Jackson and G. Porter, *Proc. R. Soc. London, Ser. A*, **260**, 13 (1961).

13) J. S. Brinen, D. D. Rosebrook, and R. C. Hirst, *J. Phys. Chem.*, **67**, 2651 (1963).

14) Z. R. Grabowski and A. Grabowska, *Z. Phys. Chem. (Neue Folge)*, **101**, 197 (1976).

15) Th. Förster, "Fluoreszenz Organischer Verbindugen," Vandenhoeck and Ruprecht (1951), p. 183.

16) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **48**, 2651 (1968).

17) E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boss, H. Prigge, and I. Seibold-Blankenstein, *Angew. Chem.*, **73**, 695 (1961).

18) R. M. Hochstrasser and C. Marzzacco, *J. Chem. Phys.*, **45**, 4681 (1966); **49**, 971 (1968).

19) C. T. Lin and J. A. Stikeleather, *Chem. Phys. Lett.*, **38**, 561 (1976).

20) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker (1973), p. 3.