The Photochemical Reduction of Nitrobenzene and Its Reduction Intermediates. X. The Photochemical Reduction of the Monosubstituted Nitrobenzenes in 2-Propanol

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(Received July 9, 1971)

The photochemical reduction of the monosubstituted nitrobenzenes has been investigated in 2-propanol under a nitrogen atmosphere. The nitrobenzenes with electron-withdrawing groups on *meta-* and *para*-positions (*p*-NO_2, *m-* and *p*-CN, *m-* and *p*-$COOC_2H_5$, *p*-$COOCH(CH_3)_2$, and *m-* and *p*-COOH) were photoreduced to the corresponding anilines, and nitrobenzene and the *para*-substituted nitrobenzenes with electron-donating groups (*p*-CH_3 and *p*-OCH_3) were photoreduced to the corresponding phenylhydroxylamines. *p*-Nitroaniline and *p*-nitrophenol were unreactive toward the photoreduction. In the experiments on the determination of the quantum yields for the nitrobenzenes' disappearance upon irradiation with a 313- or 366-nm light, it has been found that there is a linear correlation between the log-values of the relative quantum yields of the substituted nitrobenzenes and nitrobenzene and the Hammett constants, and the ρ value was $+1.5$. The results obtained suggest that the hydrogen-abstraction reaction of the photoexcited nitrobenzenes may proceed electrophilically.

Hurley and Testa2) have reported that the reactivity of the hydrogen abstraction of the protonated nitrobenzene triplet is greater than that of the unprotonated nitrobenzene triplet. Similar results have been obtained in the photoreduction of 1-nitronaphthalene in hydrochloric acid (HCl) -2-propanol (IPA) solutions.3) These results obtained by Testa *et al.* are very interesting in clarifying the mechanism of the hydrogen abstraction of the photoexcited nitro aromatic compounds. On the other hand, we ourselves have previously reported that 4-nitropyridine is not photoreduced in IPA, whereas it is reduced photochemically in a HCl-IPA solution to form 4-hydroxylaminopyridine in a quantitative yield,4) and that judging from the results of the quantum-yield measurements, the hydrogen abstraction of 4-nitropyridine in the n,π^* excited state may proceed electrophilically.1) We have also found that, when the photoreduction of the *para*-substituted nitrobenzenes is done in IPA, there is a linear correlation between the log-values of the relative quantum yields for the substituted nitrobenzenes' disappearance and the nitrobenzene and the Hammett constants (ρ : $+$).5)

In this paper, we wish to report in detail our findings on the photoreduction of the monosubstituted nitrobenzenes in IPA and to discuss the mechanism of the hydrogen-abstraction reaction of the photoexcited nitrobenzenes. Both the reporting and discussing were begun in a previous communication (Ref. 5).

Experimental

Materials. The *p*-nitrobenzonitrile6) and phenylhydroxylamine7) were prepared according to the procedures described in the literature. The monosubstituted anilines were prepared by the reduction of the corresponding substituted nitrobenzenes with zinc dust - HCl, or the reagent-grade anailines were purified prior to use. The monosubstituted phenylhydroxylamines were prepared according to the same procedures as were used in the preparation of phenylhydroxylamine.7) The other materials, commercially obtained, were purified by recrystalization or distillation.

Identification of the Products. The identification of the photoreduction products was established by comparing the UV spectra with those of authentic samples. A Hitachi 124 spectrophotometer was used to follow the progressive spectral changes in the nitrobenzenes photochemistry.

Determination of Quantum Yields. The determination of the quantum yields for the nitrobenzenes' disappearance was undertaken according to the methods of previous papers.1,5) The 366-nm light was isolated from a high-pressure 130-W mercury lamp with a Toshiba UV-D1B filter or with a combination filter of Toshiba UV-D1B and UV-35.

Results

Photoproducts of the Monosubstituted Nitrobenzenes. The progressive spectral changes were measured when 1 or 2×10^{-3} mol/*l* solutions of the nitrobenzenes in IPA were irradiated with an immersion-type 130-W high-pressure mercury lamp under a nitrogen atmosphere at room temperature. In most of the reaction, the isosbestic points were observed; therefore, it seems that the photoreaction of the nitrobenzenes in IPA proceeds quantitatively. The isosbestic points in each case were: *p*-NO_2; 233 and 294, *p*-CN; 225 and 242, *m*-CN; 265, *p*-$COOC_2H_5$; 230 and 269, *p*-$COOCH(CH_3)_2$; 231 and 268, *p*-COOH; 232 and 267, H; 244 and 288, *p*-CH_3; 253 and 302, *p*-OCH_3; 228, 266, and 366, *p*-OH; 215 and 264, and *p*-NH_2; 305 and 436 nm, respectively.

Meanwhile, the photoproducts were the corresponding substituted anilines in the photolysis of the *meta-* or *para*-substituted nitrobenzenes with electron-withdrawing groups, and were the corresponding phenylhydroxylamines in the photolysis of nitrobenzene and the *para*-substituted nitrobenzenes with electron-

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1) Part IX: S. Hashimoto, K. Kano, and K. Ueda, This Bulletin, **44**, 1102 (1971).

2) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **89**, 6917 (1967).

3) W. Trotter and A. C. Testa, *J. Phys. Chem.*, **74**, 845 (1970).

4) S. Hashimoto, K. Kano, and K. Ueda, *Tetrahedron Lett.*, **1969**, 2733.

5) S. Hashimoto and K. Kano, *ibid.*, **1970**, 3509.

6) C. S. Miller, "Organic Syntheses," Coll. Vol. III, p. 646 (1955).

7) O. Kamm, *ibid.*, Coll. Vol. I, p. 445 (1934).

donating groups, except for the p-NH_2 and p-OH derivatives. In the photolysis of p-chloronitrobenzene in IPA, no isosbestic points were observed in the UV spectrum; this suggests that the photoreaction of p-chloronitrobenzene proceeds in a complicated way. Therefore, we put off the photolysis of the halonitrobenzenes until a latter time.

Quantum Yields for the Disappearance of the Substituted Nitrobenzenes. The quantum yields for the nitrobenzenes' disappearance in IPA at 313 or 366 nm were measured. The photolysis was done under a nitrogen atmosphere at room temperature. The reaction conditions and the results obtained are summarized in Table 1.

TABLE 1. QUANTUM YIELD RESULTS FOR THE DISAPPEARANCE OF THE SUBSTITUTED NITROBENZENES IN 2-PROPANOL

$XC_6H_4NO_2$	Concn. $\times 10^3$ mol/l	Light nm	Product	Quantum yield
p-NO_2	1.00	366[a]	p-Nitroaniline	0.16
p-CN	1.03	313	p-Aminobenzonitrile	0.48[c]
m-CN	1.00	313	m-Aminobenzonitrile	0.34
p-$COOC_2H_5$	1.00	313	Ethyl p-aminobenzoate	0.15
m-$COOC_2H_5$	1.00	313	Ethyl m-aminobenzoate	0.11[c]
p-$COOCH(CH_3)_2$	0.25	313	Isopropyl p-aminobenzoate	0.15
p-COOH	1.00	313	p-Aminobenzoic acid	0.12
m-COOH	1.17	313	m-Aminobenzoic acid	0.18
H	1.10	313	Phenylhydroxylamine	0.03
p-CH_3	1.00	313	p-Hydroxylaminotoluene	0.07
p-OCH_3	0.25	313	p-Hydroxylaminoanisole	0.02
p-OH	0.50	313	—	0.00
p-NH_2	0.50	366[b]	—	0.004

a) A combination filter of Toshiba UV-D1B and UV-35 was used.

b) A filter of Toshiba UV-D1B was used.

c) In these cases, the quantum yields for the formation of the anilines were measured.

In the UV-spectrum measurements, the n,π^* absorption bands ($\log\varepsilon \leqq 2$) were observed in IPA in the 320—420 nm range for the m- and p-CN, m- and p-$COOC_2H_5$, p-$COOCH(CH_3)_2$, m- and p-COOH, H, and p-CH_3 derivatives; therefore, the reactivity of the n,π^* excited nitrobenzenes was measured by irradiation with the 313-nm light. On the other hand, since no n,π^* bands were observed in the UV spectrum for the p-OCH_3, p-OH, and p-NH_2 derivatives, the light which excites these compounds at the lowest energy was irradiated.

As Table 1 shows, the quantum yields for the disappearance of the *meta-* and *para*-substituted nitrobenzenes with electron-withdrawing groups ($\Phi_X > 0.1$) were greater than those of nitrobenzene and the *para*-substituted nitrobenzenes with electron-donating groups ($\Phi_X < 0.1$). Particularly, p-nitrophenol and p-nitroaniline were unreactive toward the photoreduction.

Solvent Effect on the Photoreduction of p-*Nitrobenzonitrile.* A solvent effect on the photoreduction of p-nitrobenzonitrile, which was most reactive toward the photoinduced hydrogen-abstraction reaction, was investigated. Table 2 shows the quantum yields for the p-nitrobenzonitrile disappearance (Φ_{CN}) upon irradiation with the 313-nm light under a nitrogen atmosphere at room temperature.

TABLE 2. SOLVENT EFFECT FOR THE PHOTOREDUCTION OF p-NITROBENZONITRILE

Concn. $\times 10^3$ mol/l	Solvent	Quantum yield
1.03	IPA	0.48
1.00	Ethanol	0.11
1.00	Cyclohexane[a]	0.00

a) It contained 10 vol% of IPA to dissolve p-nitrobenzonitrile.

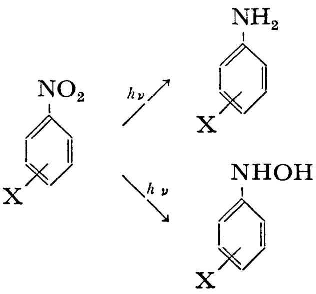
The quantum yields were influenced by the hydrogen-donating ability of the solvents. That is, the hydrogen-donating ability of the solvents in this photoreduction may classified, in decreasing order, as: IPA (secondary alcohol), ethanol (primary alcohol), and cyclohexane (parafine).

Oxygen-quenching Effect. The quenching effect by oxygen was studied in oder to clarify the state of the photoreduction.

The 1×10^{-3} mol/l solutions of p-nitrobenzonitrile and/or p-nitrotoluene in air-saturated IPA were irradiated with the 313-nm light at room temperature. In both cases, the photolysis of the nitro aromatic compounds was completely quenched by oxygen. The photoreduction of the nitrobenzenes, therefore, may proceed *via* excited triplet states.

Discussion

The Photoproducts of the Monosubstituted Nitrobenzenes. The photoproducts of the substituted nitrobenzenes were classified by substituent effects as is pictured below:



X; p-NO_2, m- and p-CN, m- and p-$COOC_2H_5$, p-$COOCH(CH_3)_2$, m- and p-COOH

X; H, p-CH_3, p-OCH_3

It has been established that nitrobenzene,[8,9] 1-

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[8] R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966).

[9] S. Hashimoto, J. Sunamoto, H. Fujii, and K. Kano, This Bulletin, **41**, 1249 (1968).

nitronaphthalene,[10] 4-nitropyridine 1-oxide,[11,12] and 4-nitropyridine[1,4] in hydrogen-donative alcohols are reduced photochemically to form the corresponding hydroxylamino compounds. However, little attention has been paid until recently to the substituent effect on the photoreduction of nitro aromatic compounds. Finnegan and Knutson[13] have reported that the photoreduction of the *meta*- and *para*-substituted nitrobenzenes in ethanol gives the corresponding anilines, as is summarized as follows:

ethyl *p*-nitrobenzoate →
  ethyl *p*-aminobenzoate (32%)
ethyl *m*-nitrobenzoate →
  ethyl *m*-aminobenzoate (24%)
t-butyl *p*-nitrobenzoate →
  t-butyl *p*-aminobenzoate (52%)
p-nitroacetophenone →
  p-aminoacetophenone (16%)
nitrobenzene →
  aniline (13%)

Since authentic samples of the *meta*- and *para*-substituted phenylhydroxylamines with electron-withdrawing groups could not be obtained, we could not clarify the process of the aniline formation. However, the *m*- and *p*-$XC_6H_4NO_2H$ radicals may also be generated in the primary steps of the aniline formation, analogous with the nitrobenzene photochemistry.[2]

Correlation between the Quantum Yields and the Hammett Constants. Photoreduction Mechanism. The data on the quantum yields shown in Table 1 indicate a quantitative correlation between the quantum yields and the Hammett constants. A plot of the log-values of the relative quantum yields ($\log \Phi_X/\Phi_H$) of the substituted nitrobenzenes and nitrobenzene *vs*. the Hammett constants[14] is shown in Figure 1. Apparently, the Hammett plots gave a straight line, and the ρ value was $+1.5$. The photochemical behavior of nitro compounds in hydrogen-donative solvents may be written as in the following sequence:

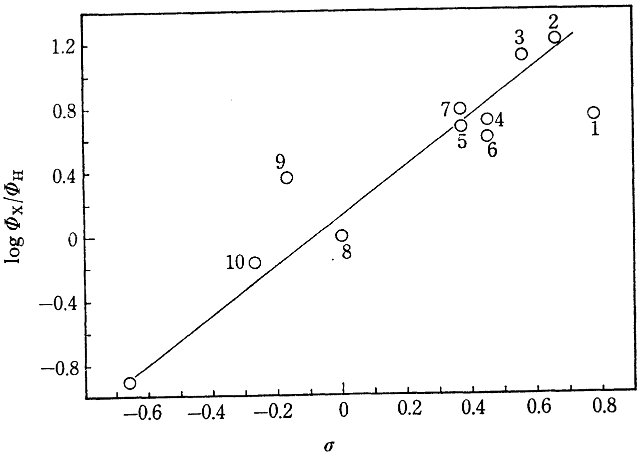


Fig. 1. Plot of $\log \Phi_X/\Phi_H$ *vs*. the Hammett constants.
1: *p*-NO_2; 2: *p*-CN; 3: *m*-CN; 4: *p*-$COOC_2H_5$; 5: *m*-$COOC_2H_5$; 6: *p*-COOH; 7: *m*-COOH; 8: H; 9: *p*-CH_3; 10: *p*-OCH_3; 11: *p*-NH_2

$N + h\nu \rightarrow N^{*1}$ excitation to a singlet (1)

$N^{*1} \xrightarrow{k_1} N$ radiationless decay (2)

$N^{*1} \xrightarrow{k_2} N^{*3}$ intersystem crossing (3)

$N^{*3} \xrightarrow{k_3} N$ radiationless decay (4)

$N^{*3} + RH \xrightarrow{k_4} NH + R$ hydrogen abstraction (5)

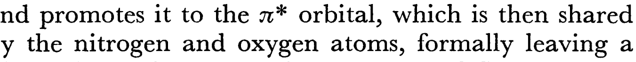
A steady-state approximation leads to this expression for the disappearance of nitro compounds:

$$\Phi = \frac{\Phi_T}{1 + [k_3/k_4(RH)]}$$

where Φ is the quantum yield for the disappearance of nitro compounds, Φ_T is the yield of the triplet, and (RH) is the concentration of the hydrogen-donative solvents. As is shown in the equation, Φ should be influenced by Φ_T, k_3, and (RH). However, our findings on the Hammett rule suggest that the only factor which governs the variation in the Φ is k_4(RH), and that the value of Φ_T and k_3 of the substituted nitrobenzenes is scarcely varied by the substituents. By the way, the electronic structure in the photoexcited states may be considerably different from that in the ground states; nevertheless, the Hammett relationship holds for the photoreduction of the nitrobenzenes in IPA. These findings suggest that the hydrogen-abstraction reaction of the photoexcited nitrobenzenes proceeds electrophilically and that the reactivity is governed by the electron density of the nitro groups in the ground states.

The photoreduction of the nitrobenzenes was quenched by oxygen; therefore, the photochemical hydrogen-abstraction reaction might proceed from the n,π^* triplet states (except for the *p*-OCH_3, *p*-NH_2, and *p*-OH derivatives).

The n,π^* transition of the nitro group may be pictured as follows:[15]



(I) (II) (III)

Ground state n, π^* Excited state

•: π electron; ∘: *sp* electron; *y*: p_y electron

Structures (I) and (III) imply that a n,π^* excited state may be found to exhibit biradical properties. On the other hand, as Structure (II) shows, n,π^* excitation removes an electron from the oxygen atom and promotes it to the π^* orbital, which is then shared by the nitrogen and oxygen atoms, formally leaving a 1/2 positive charge on the oxygen. If Structure (I) or (III) participates in the photoreduction, the photoreduction of the nitrobenzenes is similar to the hydro-

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[10] S. Hashimoto and K. Kano, *Kogyo Kagaku Zasshi*, **72**, 188 (1969).

[11] C. Kaneko, S. Yamada, I. Yokoe, N. Hata, and Y. Ubukata, *Tetrahedron Lett.*, **1966**, 4729.

[12] N. Hata, E. Okutsu, ans I. Tanaka, This Bulletin, **41**, 1769 (1968).

[13] R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **90**, 1670 (1968).

[14] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

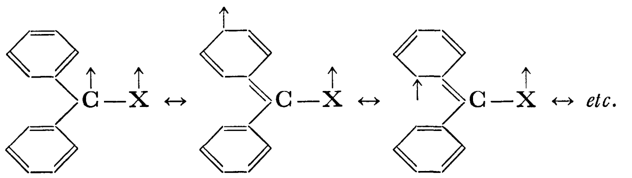
[15] H. A. Morrison, "The Chemistry of Nitro and Nitroso Compounds," ed. by H. Feuer, Interscience Publications, New York, N. Y. (1969) p. 169.

gen abstraction of the R·radical, which is well-known to proceed electrophilically. Meanwhile, if Structure (II) is an active species, our mechanism can be interpreted on the basis of this structure, because the electron affinity of the nitro groups increases in Structure (II).

The electrophilic hydrogen-abstraction mechanism is supported by the results on the photoreduction of 4-nitropyridine in the HCl-IPA solutions.[1)]

It seems that the photoreduction mechanism of the nitrobenzenes is similar to that of the benzophenones. Porter *et al.*[16)] have, on the basis of the quantum yields and spectroscopic data, reported that the hydrogen abstraction of the benzophenone triplet, the state of which are classified as n,π^*, π,π^*, and charge-transfer (CT) states, proceeds electrophilically. Meanwhile, Walling and Gibian[17)] have found that the Hammett relationship holds for the photoreduction of benzophenone in substituted toluenes ($\rho=-1.15$).

On the other hand, Rosenberg and Servé[18)] have reported that, judging from the results of the Stern - Volmer quenching studies, the rate constant for the triplet hydrogen abstraction of 1,1-diphenylethylene (DPE) in IPA is 1.4×10^9 mol^{-1} l sec^{-1}, which is considerably greater than the corresponding value reported for benzophenone, 10^6 mol^{-1} l sec^{-1}.[19)] They have suggested that the electron repulsion between the unpaired electrons in the triplet states of DPE and benzophenone strongly induces the delocalization of one electron, so that the ability for the hydrogen abstraction of the two in the triplet states is similar to that of free radicals, such as alkyl and alkoxy radicals.[17,20)] In other words, their interpretation means that the localization of one electron on the terminal carbon and/or oxygen atoms is important for the effective photoreduction.



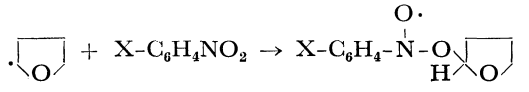
X=O, CH$_2$

Our results will be interpreted in terms of the mechanism postulated by Rosenberg and Servé. That is, the substituents on the *ortho*- and/or *para*-positions of the nitrobenzenes will facilitate the delocalization of one electron in the triplet states; therefore, the *ortho*- and *para*-substituted nitrobenzenes triplet may act as free radicals. In fact, the quantum yields for the disappearance of the *para*-substituted nitrobenzenes were greater than those of nitrobenzene (except for the p-OCH$_3$, p-NH$_2$, and p-OH derivatives). Particularly, the relative quantum yield of p-nitrotoluene ($\sigma=-0.170$) was 2.3. However, in the photolysis of the *meta*-derivatives with electron-withdrawing groups, the character of which as free radicals may be weaker than that of the *ortho*- and *para*-derivatives in their excited states, the quantum yields of the photoreduction are markedly greater than those of nitrobenzene. This suggests that the electron distribution of the nitro groups in the photoexcited states or ground states is an important factor in dominating the hydrogen-abstraction reaction of the photoexcited nitrobenzenes.

Hurley and Testa[2)] have found that the nitrobenzene triplet is protonated in the higher acidity range, and that the reactivity toward the hydrogen abstraction of the protonated nitrobenzene triplet is greater than that of the unprotonated nitrobenzene triplet. This finding can be interpreted in terms of the electrophilic hydrogen-abstraction mechanism. That is, the positive charge of a proton which adds to the nitro group promotes it to one oxygen atom of the nitro group, so that the electron affinity of the nitro group is enhanced; the photoinduced abstraction of hydrogen may, therefore, effectively proceed. The photochemistry of 1-nitronaphthalene in the HCl - IPA solutions[3)] may be understood in terms of the same interpretation.

$$\mathrm{C_6H_5NO_2H^{+*T} + (CH_3)_2CHOH \rightarrow C_6H_5N\dot{O}_2H + H^+ + (CH_3)_2\dot{C}OH}$$

Meanwhile, Janzen and Gerlock[21)] have reported, in their paper on substituent effects on the photochemistry of the nitro aromatic compounds in tetrahydrofuran, as studied by ESR spin-trapping techniques, that the photolysis of the substituted nitrobenzenes with electron-withdrawing groups gives the correspondingly-substituted nitroxide radicals (IV), whereas most of the substituted nitrobenzenes with electron-donating groups do not give the (IV) radical except for p-phenyl-, m- and p-methyl-, p-ethyl-, p-isopropyl-, and p-phenoxynitrobenzenes. The results of the studies of the substituent effects by ESR seem to be connected with our findings: the quantum yields for the disappearance of the *meta*- and *para*-substituted nitrobenzenes with electron-withdrawing groups are greater than those of the *para*-substituted nitrobenzenes with electron-donating groups.



$$\cdot\mathrm{C_4H_7O} + \mathrm{X\text{-}C_6H_4NO_2} \rightarrow \mathrm{X\text{-}C_6H_4\text{-}\overset{O\cdot}{N}\text{-}O\text{-}C_4H_7O}$$

(IV)

Photoreduction of p-*Nitroaniline and* p-*Nitrophenol.* p-Nitroaniline and p-nitrophenol were unreactive toward the photolysis in IPA; the quantum yields were 0.004 and 0.00 respectively.

The absorption maximum of p-nitroaniline at 322 nm ($\varepsilon_{\max}=1.4\times10^4$) in n-hexane (containing 0.5 vol% of IPA to disolve p-nitroaniline) shifted to 377 nm ($\varepsilon_{\max}=1.6\times10^4$) in IPA, and the solvent shift

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[16)] G. Porter and P. Suppan *Trans. Faraday Soc.*, **61**, 1664 (1965), and other references cited therein.

[17)] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965).

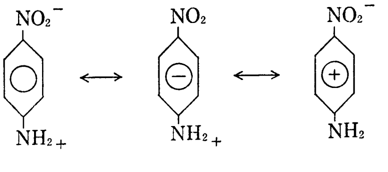
[18)] H. M. Rosenberg and P. Servé, *ibid.*, **92**, 4746 (1970).

[19)] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); S. G. Cohen and W. V. Sherman, *J. Amer. Chem. Soc.*, **85**, 1642 (1963).

[20)] A. Padua, *Tetrahedron Lett.*, **1964**, 3465; S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, **87**, 2996 (1965).

[21)] E. G. Janzen and J. L. Gerlock, *J. Amer. Chem. Soc.*, **91**, 3108 (1969).

was +4500 cm^{-1} (the + sign means an increase in the polarity on excitation).[16] This enormous shift shows that the polarity of the molecule is greatly increased in the excited state, and it suggests that the absorption at 377 nm in IPA is an intra-molecular charge transfer (CT) band. In fact, the CT band of *p*-nitroaniline has been observed by Tanaka[22] and Godfrey.[23] The CT configuration of *p*-nitroaniline may pictured as follows:



Therefore, if the lowest excited energy level of *p*-nitroaniline is the CT triplet, the electron density of the nitro group may be greatly increased, so that the electrophilic attack will be made very difficult.

Therefore, the photolysis of *p*-nitroaniline in a HCl-IPA solution was carried out in order to clarify the state of the hydrogen abstraction.

A 5×10^{-4} mol/*l* solution of *p*-nitroaniline in a 2.4 mol/*l* HCl solution with 50% IPA-water was irradiated by a 366-nm light under a nitrogen atmosphere at room temperature. The quantum yield for the disappearance of *p*-nitroaniline was 0.004 in IPA, whereas it was 0.03 in the HCl-IPA solution. The increase in the quantum yield in the HCl-IPA solution suggests that the lowest excited state of *p*-nitroaniline hydrochloride is the n,π^* triplet, which is more reactive toward photoreduction than the CT triplet, or that the CT state of *p*-nitroaniline is protonated and has an increased reactivity. This photoreductive behavior of *p*-nitroaniline is similar to that of *p*-dimethylaminobenzophenone in an IPA and/or an IPA-HCl solution.[24] However, *p*-nitroaniline was unreactive in cyclohexane, and in this case, the quantum yield for the disappearance of *p*-nitroaniline was nearly zero.

By the way, *p*-nitrophenol was also completely unreactive toward the photoreduction in IPA. Proter and Suppan[16] have reported that *p*-hydroxybenzophenone in IPA is efficiently deprotonated in the excited singlet and triplet states, and that the lowest excited state of *p*-hydroxybenzophenone is the CT triplet; therefore, the abstraction of hydrogen occurs ineffectively in the photolysis of *p*-hydroxybenzophenone in IPA. The deprotonation of *p*-nitrophenol has not yet been investigated; however, it may be reasonable to conclude that the lowest excited state of *p*-nitrophenol in IPA is the unreactive CT state, because an absorption maximum at 289 nm in *n*-hexane (containing 0.05 vol% of IPA to dissolve *p*-nitrophenol) shifted to 312 nm in IPA, and the solvent shift was enormous (+2500 cm^{-1}).

Photochemical Partial Reduction of p-*Dinitrobenzene.* As has been described above, the *meta*- and *para*-substituted nitrobenzenes with electron-withdrawing groups were relatively reactive toward the photoreduction in IPA, whereas *p*-nitroaniline was unreactive. These findings may be useful for the photochemical partial reduction of *p*-dinitrobenzene to afford *p*-nitroaniline.

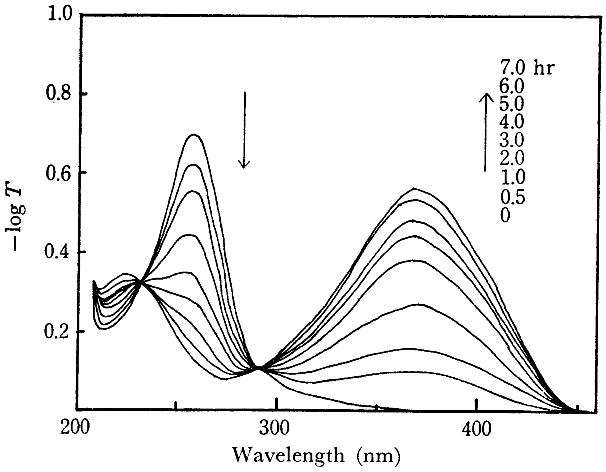


Fig. 2. Progressive spectral change of the photolysis of *p*-dinitrobenzene in IPA.

Figure 2 shows the progressive spectral change when a 2×10^{-3} mol/*l* solution of *p*-dinitrobenzene in IPA was irradiated with a high-pressure 130-W mercury lamp under a nitrogen atmosphere at room temperature. The absorption spectrum of *p*-dinitrobenzene decreased progressively in intensity, and a new absorption band of *p*-nitroaniline with its maximum at *ca.* 370 nm appeared. The isosbestic points were observed at 233 and 293 nm; therefore, the photochemical partial reduction of *p*-dinitrobenzene may proceed quantitatively.

Meanwhile, the n,π^* band of *p*-dinitrobenzene with a maximum at *ca.* 350 nm ($\varepsilon=100$) was observed in IPA. Then a 1×10^{-3} mol/*l* solution of *p*-dinitrobenzene in IPA was irradiated by a 366-nm light under a nitrogen atmosphere at room temperature; the quantum yield for the disappearance of *p*-dinitrobenzene was thus obtained as 0.16. This value ($\log \Phi_X/\Phi_H$) greatly deviates from the Hammett plot, as is shown in Figure 1. This finding may be interpreted in terms of the inner-filter effect caused by *p*-nitroaniline. That is, the intense CT band with a maximum at 377 nm ($\varepsilon_{max}=1.6\times10^4$) of *p*-nitroaniline produced is absorbed near the 350-nm light, thus promoting the $n\rightarrow\pi^*$ transition of *p*-dinitrobenzene.

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[22] J. Tanaka, *Nippon Kagaku Zasshi*, **79**, 1373 (1958); J. Tanaka, This Bulletin, **36**, 833 (1963).

[23] M. Godfrey and J. N. Murrell, *Proc. Roy. Soc.* **A278**, 71 (1964).

[24] S. G. Cohen and M. N. Siddiqui, *J. Amer. Chem. Soc.*, **89**, 5409 (1967).