Photochemistry of Heterocyclic Compounds. VI. The Photochemical Behavior of Phenazine in Hydroxylic Solvents[1)]

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The photochemical behavior of phenazine in acidified hydroxylic solvents varied with the concentration of acids present in the solutions. Irradiation of phenazine in an aqueous phosphoric acid afforded a 1: 1 mixture of phenazinium and 1-hydroxyphenazinium cation radicals which were converted to a mixture of phenazine and 1-hydroxyphenazine. Irradiation in moderately strongly acidified alcohols (0.1—1.0 M HCl in alcohols) or in acetic acid containing 0.1 M *p*-toluenesulfonic acid yielded a 1: 1 mixture of phenazine and the corresponding 1-alkoxyphenazines or 1-acetoxyphenazine after work-up of the reaction mixture. On the other hand, irradiation in a very strongly acidified methanol (5.6—9.6 M HCl in methanol) gave only the phenazinium cation radical. Mechanistic studies revealed that in the moderately strongly acidified media the reaction proceeds through a solvent-addition to the excited singlet phenazinium monocation, and in the very strongly acidified methanol the reaction proceeds through an electron transfer from the solvent to the excited singlet phenazinium dication.

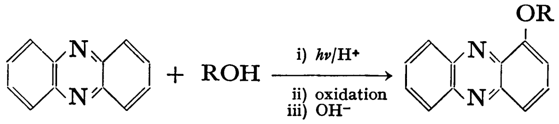
The photochemistry of phenazine has received considerable attention. Toromanoff[2)] has shown that irradiation of phenazine in deaerated alcohols gives 5,10-dihydrophenazine. Koizumi and co-workers[3)] have proposed that the photoreduction of phenazine in alcohols occurs through a hydrogen abstraction from the higher n, π^* triplet state. However, Davis and co-workers[4)] have presented evidence that a reactive state of the photoreduction is the n, π^* singlet state.

Recently, Bailey, Roe, and Hercules[5)] have studied the photochemistry of phenazine in acidified methanol. They have concluded on the basis of spectroscopic evidence that in very weakly acidified media (acetate buffers in methanol), phenazine is reduced to 5,10-dihydrophenazine through the lowest n, π^* singlet state. They have also shown that in moderately strongly acidified media (0.1—1.0 M HCl in methanol), phenazine gives the green phenazinium cation radical, which is produced by the reaction of 5,10-dihydrophenazine with phenazinium cation, through the lowest excited singlet state. However, the structure of the photoproducts was deduced only from electronic and ESR spectra of the reaction mixtures, and no unequivocal evidence for the structures was given in their investigation.

We have recently investigated the photochemistry of phenazine in detail and have found that the photochemical behavior of phenazine in hydroxylic solvents is strongly dependent on the concentration of acids present in the solutions. For example, we obtained a mixture of phenazinium and 1-methoxyphenazinium cation radicals upon irradiation of phenazine in moderately strongly acidified methanol (0.1—1.0 M HCl in methanol). However, in the photoreaction in very strongly acidified methanol (5.6—9.7 M HCl in methanol), the photoreduction took place to give the phenazinium cation radical. In this paper, the results accumulated so for are summarized and the mechanisms are proposed on the basis of informations obtained from kinetic studies of these photochemical reactions.

Results

Photoreactions in Moderately Strongly Acidified Solutions. When a 2.8×10^{-3} M solution of phenazine (I) in 2 M aqueous phosphoric acid was irradiated with a high-pressure mercury lamp under nitrogen atmosphere, a green solution containing green precipitates was produced. Oxidation of the green reaction mixture with air or other oxidizing agents, followed by neutralization of the resulting solution, gave 1-hydroxyphenazine (IIa) accompanied by the starting material. Irradiation of I in various alcohols acidified with 0.1 M *p*-toluenesulfonic acid and similar work-up of the reaction mixture afforded a mixture of I and the corresponding 1-alkoxyphenazines (IIb—IId). Similarly, the photoreaction of I in acetic acid containing *p*-toluenesulfonic acid yielded 1-acetoxyphenazine (IIe). These photochemical solvent-addition reactions were not observed upon irradiation in the absence of acids. The results are summarized in Table 1.



IIa, R=H
b, R=CH_3
c, R=C_2H_5
d, R=i-C_3H_7
e, R=CH_3CO

The structure of the photoproducts was confirmed by comparison with the respective authentic samples or by the spectroscopic data.

Quantitative studies of these photoreactions were then preformed. When I was irradiated in 2 M phosphoric acid, the yield of IIa increased with increasing irradiation time.

However, the molar ratio of IIa to I in the reaction mixture reached a plateau, which was very close to unity, upon prolonged irradiation under nitrogen atmosphere as shown in Table 1. Irradiation under air brought about a decrease in the recovery of I (14%) and an increase in the yield of IIa (81%). IIa was surprisingly stable under the reaction conditions; ir-

Table 1. Photochemical addition of solvents[a)]

Solvents	ml	Irrad. time, hr	Recovered starting material, %	Compd.	Products yield,[b)] %	Ratio[c)]
H_2O, 2M H_3PO_4	200	7	52	IIa	45	0.9
H_2O, 2M H_3PO_4	200	48	53	IIa	47	0.9
H_2O, 2M HCl	50	7	76	IIa	19	0.3
MeOH, 0.1M TsOH[d)]	50	7	65	IIb	26	0.4
MeOH, 0.1M HCl	50	7	57	IIb	32[e)]	0.6
EtOH, 0.1M TsOH[d)]	50	7	70	IIc	16	0.2
i-PrOH 0.1M TsOH[d)]	100	7	82	IId	4	0.05
AcOH, 0.1M TsOH[d)]	50	7	75	IIe	19[f)]	0.2

a) A 100 mg of phenazine was irradiated under N_2 atmosphere. b) Based on total amount of the starting material. c) The molar ratio of the product to phenazine found in the reaction mixture. d) *p*-Toluenesulfonic acid. e) Irradiation was carried out in the presence of air. f) The yield of IIe was estimated as that of IIa obtained by hydrolysis.

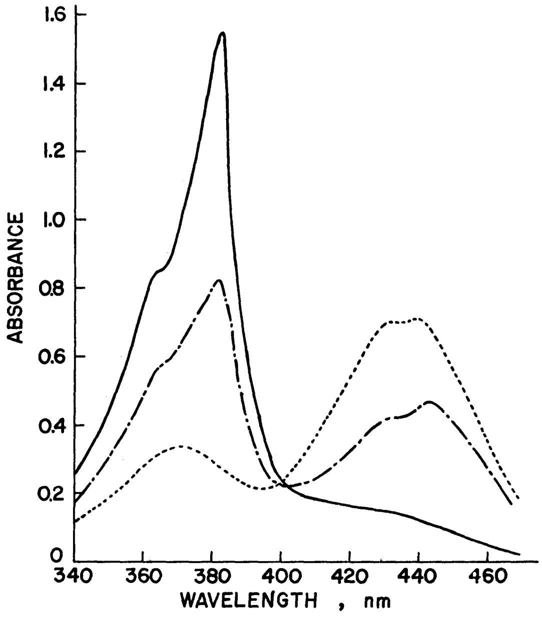


Fig. 1. Spectral change during irradiation of 7.0×10^{-5}M solution of phenazine in 2 M H_3PO_4: ——, before irradiation; ·····, irradiation for 20 min; ------, irradiation for 1.5 hr.

radiation of IIa in 2 M phosphoric acid for 7 hr under air resulted in the recovery of the starting material in a quantitative yield.

The change in the absorption spectrum during the photoreaction was also examined. A solution of I in 2 M phosphoric acid in a quartz cell was irradiated after degassing by a freeze-pump-thaw cycle method. The result is shown in Fig. 1. The spectral change almost ceased after irradiation for 1.5 hr. The spectrum recorded after irradiation for 1.5 hr was identical in shape with that of phenazinium cation radical (III) prepared by the method similar to that of Fellion and Uebersfeld.[6)] Furthermore, the green precipitates obtained by the photoreaction displayed the same IR and electronic spectra as those of the green species which was produced by treatment of a mixture of I and IIa in dioxane containing 2 M phosphoric acid with an aqueous solution of sodium hydrosulfite (the green species produced by this treatment in the dark gave a mixture of I and IIa after oxidation and neutralization).

The ESR spectrum of the green precipitate obtained by the photoreaction exhibited the same *g*-value (2.003) as that of the known ESR spectrum of III previously reported.[7)]

These observations strongly suggest that the product primarily formed by the photoreaction of I in 2 M phosphoric acid consists of a 1: 1 mixture of III and 1-hydroxyphenazinium cation radical (IV), which affords I and IIa upon oxidation and neutralization. The green species, the primary products, obtained by the photoreactions of I in solvents other than water are therefore supposed to be a 1: 1 mixture of III and the respective 1-alkoxyphenazinium cation radicals (V) or 1-acetoxyphenazinium cation radical (VI).

Photoreactions in Very Strongly Acidified Solutions. When I was irradiated in HCl-saturated methanol, the green solution was obtained. The absorption spectrum of this green solution was very similar to that obtained by the photoreaction of I in 0.1 M HCl–methanol. However, work-up of this green solution resulted in a complete recovery of the starting material and no IIb could be detected. These results indicate that in HCl-saturated methanol, the photoreduction of I to give III takes place preferentially over the photochemical solvent-addition reaction.

Mechanistic Studies. Deoxygenated solutions of I in water or methanol containing various concentrations of acids in a 1 cm optical cell were irradiated with a high-pressure mercury lamp fitted with a cut-off filter which transmitted >310 nm light. At appropriate time intervals, the spectra of the solutions were recorded.

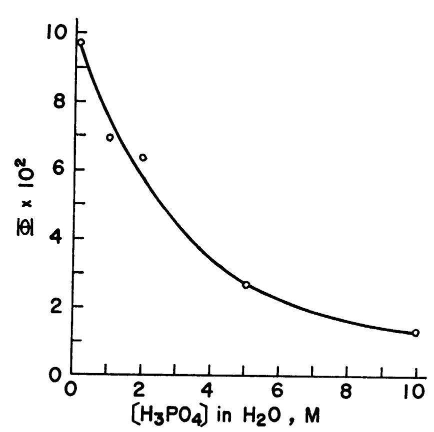


Fig. 2. Quantum yields for the formation of a 1 : 1 mixture of III and IV as a function of the acid concentrations upon irradiation of I in aqueous phosphoric acid. Initial concentrations of I were 7.22×10^{-5}—6.07×10^{-5}M. The quantum yield at 7.0×10^{-5}M of I in 0.1 M H_3PO_4 was estimated by using the relationship of Eq. (9), coupled with the quantum yields in Table 2 ($\Phi=0.08$ at 4.21×10^{-5}M of I and $\Phi=0.071$ at 3.25×10^{-5}M of I).

For each reaction the 380 nm band of I decayed with production of the 430 nm band as has been shown in Fig. 1. For calculations of the rates of formations of the products, it was considered that the 430 nm band was of a mixture of the cation radicals (III+IV or III+V) or of the single phenazinium cation radical (III) depending on the concentration of acids. The rates were then converted to the quantum yields by use of the potassium ferrioxalate actinometer.8)

Photoreactions in Aqueous Media. Variation of the quantum yields for the formation of a mixture of the cation radicals III and IV with the concentrations of phosphoric acid was investigated. The quantum yields decreased with increase of the concentrations of acid in a fashion depicted in Fig. 2. Dependence of the quantum yields on the concentrations of I in 2 M phosphoric acid was also studied. The results are summarized in Table 2. A plot of reciprocal quantum yields *vs.* reciprocal concentrations of I gave a straight line as shown in Fig. 3. No quenching was observed with air under a wide variety of reaction conditions (Table 2).9)

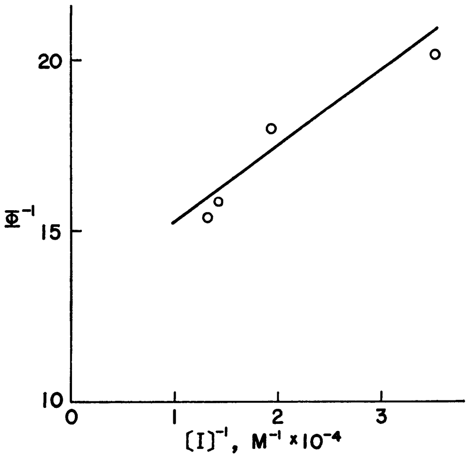


Fig. 3. Dependence of the quantum yields for the formation of a 1 : 1 mixture of III and IV on the concentrations of I in 2 M H_3PO_4.

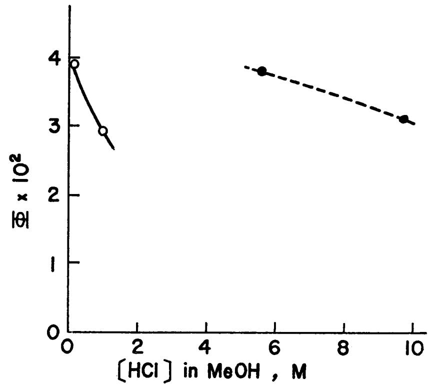


Fig. 4. Quantum yields for the product formation as a fuction of the acid concentrations upon irradiation of I in HCl–methanol: ——, the product is a 1 : 1 mixture of III and Va; ------, the product is III.

TABLE 2. QUANTUM YIELDS FOR HTE FORMATION OF A 1 :1 MIXTURE OF THE CATION RADICALS III AND IV UPON IRRADIATION OF I IN AQUEOUS PHOSPHORIC ACID

Concn. of I, M	Concn. of H_3PO_4, M	Quantum yield
4.21×10^{-5}	0.1	0.080
3.25×10^{-5}	0.1	0.071
7.22×10^{-5}	1.0	0.069
7.67×10^{-5}	2.0	0.065
7.00×10^{-5}	2.0	0.063
7.00×10^{-5}	2.0	0.062
5.15×10^{-5}	2.0	0.056
2.85×10^{-5}	2.0	0.049
6.07×10^{-5}	5.0	0.027
6.80×10^{-5}	10.0	0.013
6.07×10^{-5}a)	10.0	0.013

a) Irradiation was carried out in the presence of air.

Photoreactions in Acidified Methanol. The quantum yields for the formation of the cation radicals were measured as a function of the concentrations of HCl. The result is shown in Fig. 4. The quantum yields varied with variation of the acid concentrations in such

TABLE 3. QUANTUM YIELDS FOR THE FORMATION OF THE PHOTOPRODUCTS UPON IRRADIATION OF I IN ACIDIFIED METHANOL

Concn. of I, M	Concn. of HCl, M	Additive, M	Quantum yield
6.22×10^{-5}	0.1		0.039a)
7.56×10^{-5}	0.1	1,2-DBE,c) 0.01	0.041a)
6.36×10^{-5}	1.0		0.029a)
6.36×10^{-5}	1.0	1,2-DBE,c) 0.01	0.029a)
6.73×10^{-5}	5.6		0.038b)
3.66×10^{-5}	5.6		0.047b)
6.42×10^{-5}	9.7		0.031b)
6.11×10^{-5}	9.7	1,2-DBE,c) 0.01	0.032b)

a) The product is a 1 : 1 mixture of the cation radicals III and Va. b) The product is phenazinium cation radical III. c) 1,2-DBE represents 1,2-dibromoethane.

a manner that a minimum is produced at an intermediate concentration of the acid. Furthermore, the quantum yields for the formation of III at the high concentration of the acid (5.6 M HCl in methanol) decreased with increase of the concentrations of I as shown in Table 3. This result is in sharp contrast with the result of the photoreactions in 2 M phosphoric acid, where the photoproduct was the mixed cation radicals and the quantum yields for their formation increased with increase of the concentrations of I.

Quenching experiments employing 1,2-dibromoethane as a quencher were also performed. Essentially no quenching was observed as recognized from the results shown in Table 3.

Discussion

Phenazine (I) undergoes the solvent-addition reaction or the reduction reaction, depending on the concentration of acids, upon irradiation in acidified hydroxylic solvents.

$$\mathrm{P} + \mathrm{H}^+ \xrightarrow{h\nu,\ k_1} {}^1\mathrm{PH}^{+*} \text{ (excitation and protonation)} \qquad (1)$$

$$\mathrm{PH}^+ \xrightarrow{h\nu,\ k_2} {}^1\mathrm{PH}^{+*} \text{ (excitation)} \qquad (2)$$

$${}^1\mathrm{PH}^{+*} + \mathrm{H}^+ \xrightarrow{k_3} {}^1\mathrm{PH}_2{}^{2+*} \text{ (excited state protonation)} \qquad (3)$$

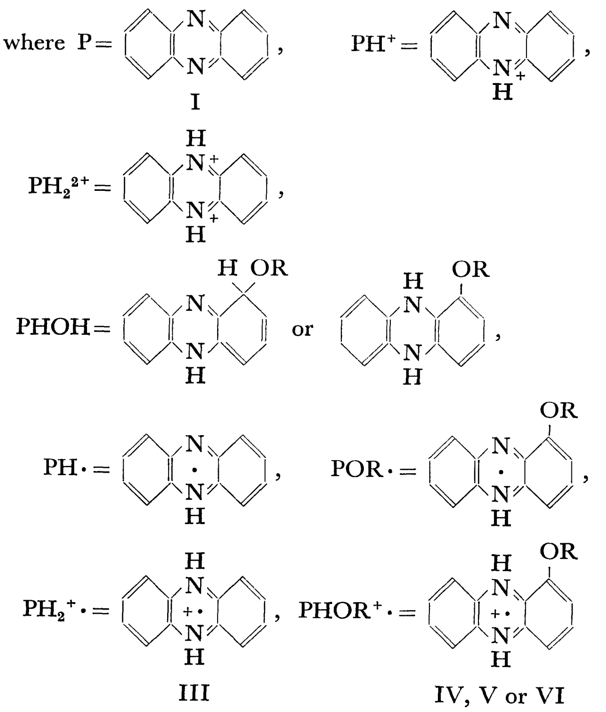
$${}^1\mathrm{PH}^{+*} + \mathrm{ROH} \xrightarrow{k_4} \mathrm{PHOR} + \mathrm{H}^+ \text{ (photoreaction; solvent-addition)} \qquad (4)$$

$$\mathrm{PHOR} + \mathrm{P} \xrightarrow{k_5} \mathrm{PH}\cdot + \mathrm{POR}\cdot \text{ (radical formation)} \qquad (5)$$

$$\mathrm{PHOR} + \mathrm{PH}^+ \xrightarrow{k_6} \mathrm{PH}\cdot + \mathrm{POR}\cdot + \mathrm{H}^+ \text{ (radical formation)} \qquad (6)$$

$$\mathrm{PH}\cdot + \mathrm{H}^+ \xrightarrow{k_7} \mathrm{PH}_2{}^+\cdot \text{ (radical protonation)} \qquad (7)$$

$$\mathrm{ROR}\cdot + \mathrm{H}^+ \xrightarrow{k_8} \mathrm{PHOR}^+\cdot \text{ (radical protonation)} \qquad (8)$$



Scheme 1.

Photoreactions in Moderately Strongly Acidified Media. The pathway represented in Scheme 1 is proposed for the photochemical solvent-addition reactions which occur upon irradiation of I in moderately strongly acidified hydroxylic solvents (in Scheme 1, all the intersystem crossing and radiationless deactivation processes of excited species, which have no immediate relation to the chemical reactions, are omitted).

The pK_a of the ground state of I has been reported to be 1.23 in water[10] and to be 4.5 in methanol.[5] Thus, in aqueous phosphoric acid (the first pK_a of phosphoric acid in water is 1.04 at 18 °C), I exists either in the neutral form or in the form of monoprotonated phenazinium cation (PH$^+$). In acidified methanol containing HCl more than 0.1 M, I exists almost exclusively in the form of PH$^+$.

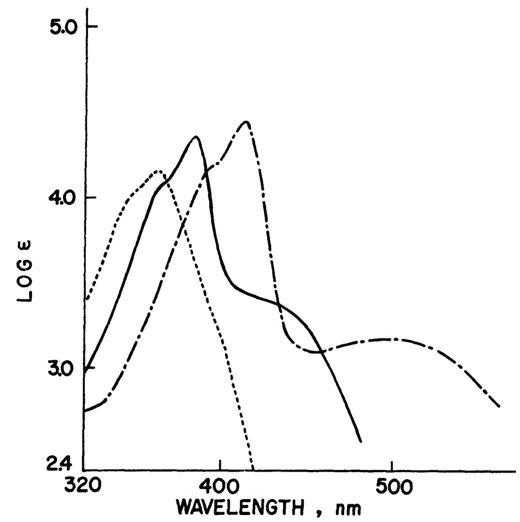


Fig. 5. Absorption spectra of phenazine: ------, in methanol; ——, in aqueous 10 M phosphoric acid; -·-·-·-, in concentrated sulfuric acid.

The pK_a* of the lowest excited singlet state of I is expected to be much higher than the corresponding ground state pK_a judging from the fact that the absorption spectrum of I shifts to longer wavelength in acidified media than in neutral media as shown in Fig. 5. It is therefore reasonable to suppose that in the excited singlet state I exists predominantly in the form of phenazinium cation even in relatively weakly acidified media.[11]

We thus propose that the excited monoprotonated phenazinium cation (PH^{+*}) is a reactive species for the photochemical solvent-addition reactions to I. This proposal was derived further from the following arguments.

Firstly, the nonprotonated species is immediately disqualified as a reactive species from the fact that the solvent-addition reactions did not take place in neutral media. Secondly, let's consider variation of proportion of PH^{+*} as a function of the acid concentration. The proportion of PH^{+*} will decrease with increasing the proportion of the excited diprotonated species (PH$_2{}^{2+*}$) which would presumably be produced in the presence of the higher concentrations of acids (see also later). Therefore, if PH^{+*} is the reactive species, the quantum yield for the formation of a mixture of the cation radicals, $PHOR^{+}\cdot$ and $PH_2^{+}\cdot$, is expected to decrease at such higher concentrations of acids as to bring the formation of PH_2^{2+*} predominant. This is exactly the results shown in Figs. 2 and 4. Quenching experiments performed by employing 1,2-dibromoethane and air as quenchers (Tables 2 and 3) suggest that the excited singlet is the reactive state, which is consistent with the conclusion reached by Bailey and co-workers[5] for the photoreactions of I in acidified methanol. An application of the steady state assumption regarding the transient species, ${}^1PH^{*1}$, ${}^1PH_2^{2+*}$, PHOR, $PH\cdot$, and $POR\cdot$, in Scheme 1 leads to the relationship of Eq. (9) under the conditions where the concentration of acids is constant:

$$1/\Phi = A/[P] + B \tag{9}$$

where [P] is the concentration of I present in the reaction mixture, which will be roughly equal to the concentration of I initially added, and the coefficients, A and B, are of constant values. The relationship depicted in Fig. 3 is in accordance with this equation.

Photoreactions in Very Strongly Acidified Media. The photoreaction of I in methanol containing HCl more than 5.6 M gave only phenazinium cation radical, $PH_2^{+}\cdot$. A proposed mechanism for this photoreduction is shown in Scheme 2 (in this scheme, all the intersystem crossing and deactivation processes of the excited species, which have no immediate relation to the chemical reactions, are also omitted, as does in Scheme 1).

$$PH^{+} \xrightarrow{h\nu,\, k_2} {}^1PH^{+*} \text{ (excitation)} \tag{2}$$

$$^1PH^{+*} + H^{+} \xrightarrow{k_3} {}^1PH_2^{2+*} \text{ (excited state protonation)} \tag{3}$$

$$^1PH_2^{2+*} + PH^{+} \xrightarrow{k_{10}} 2PH^{+} + H^{+}$$
$$\text{(quenching of the excited protonated species)} \tag{10}$$

$$^1PH_2^{2+*} + CH_3OH \xrightarrow{k_{11}} PH_2^{+}\cdot + CH_3OH^{+}\cdot$$
$$\text{(photoreaction; electron transfer)} \tag{11}$$

where all symbols are the same as those in Scheme 1.

Scheme 2.

The absorption spectrum of I in methanol containing 9.7 M HCl indicated that a predominant form of I in its ground state in this medium was PH^{+}. But the pK_a^{*} for the second protonation at the excited singlet state to form the excited diprotonated phenazinium dication (PH_2^{2+*}) is again expected to be much higher than the corresponding second pK_a at the ground state judging from the magnitude of the spectral shift observed in the concentrated sulfuric acid (see Fig. 5). Therefore, the excited phenazine may possibly exist in the form of PH_2^{2+*} at higher concentrations of acids.

The electron transfer reaction to PH_2^{2+*} from solvent would produce phenazinium cation radical ($PH_2^{+}\cdot$) as represented in the reaction (11) of Scheme 1. The observation that in the presence of higher concentrations of acids, $PH_2^{+}\cdot$ was produced only in methanol but not in water strongly supports this electron transfer mechanism; the electron transfer from water to the substrate would be unfavorable under the reaction conditions. Noteworthy is in this connection the behavior of diazaheteroaromatic diquaternary salts. Curphey[13] has reported that 1,4-diethylpyrazinium difluoroborate is converted to its cation radical upon dissolving in ethanol. This observation implies that dications of diazaheteroaromatic compounds possess enough ability to abstract an electron from an alcohol even in the dark owing to their high electron deficiency caused by an accumulation of two positive charges.

The result that the quantum yields for the formation of $PH_2^{+}\cdot$ increased with decrease of the initial concentrations of I suggests that PH_2^{2+*} may effectively be quenched by PH^{+}.

Lack of quenching by 1,2-dibromoethane again suggests that the excited singlet state (${}^1PH_2^{2+*}$) is a reactive state for the photochemical reduction of I in very strongly acidified methanol.

Experimental

Unless otherwise indicated, irradiations were carried out with a Taika 100 W high-pressure immersion mercury lamp at room temperature.

Materials. Phenazine (I) was prepared by the method of Wohl and Aue.[14] Purification was performed by column chromatography on acidic alumina using benzene as an eluent, followed by recrystallization from EtOH, mp 171—172 °C.

All other chemicals were of commercial origin and were usually used after purification by distillation or recrystallization. Water was purified by redistillation of deionized water.

Preparation of the Authentic Samples. 1-Hydroxyphenazine (IIa), mp 156—158 °C, and 1-methoxyphenazine (IIb), mp 166—167 °C, were prepared by the method of Surrey.[15] 1-Acetoxyphenazine (IIe) was prepared by the reaction of IIa and acetic anhydride in pyridine, and purified by recrystallization from MeOH, mp 119—120 °C; NMR ($CDCl_3$) δ 2.58 (s, 3H, $-CH_3$), 7.50—8.38 (m, 7H, aromatic H).

The structure of the photoproducts was identified by the mixed melting point test and by the comparison of IR spectra of the products with those of the corresponding authentic samples unless otherwise indicated.

Irradiation of I in Aqueous 2 M H_3PO_4 Solution. I (100 mg, 0.56 mmol) in aqueous 2 M H_3PO_4 solution (200 ml) was placed in a quartz vessel and N_2 was bubbled for 20 min. Irradiation was then carried out for 7 hr with bubbling N_2. Green solid (A) deposited was collected by filtration. The filtrate was allowed to stand overnight under air, while the color of the solution turned from green to red. The solution was then neutralized with Na_2CO_3 and extracted with ether. The ether solution was extracted with 10% NaOH until no more purple color moved to aqueous layer, and then the ether layer was dried over Na_2SO_4. Distillation of the ether gave 17 mg of the unchanged I. The combined aqueous extracts were made faintly acid with dilute HCl, and again extracted with ether. The ether extract was dried over Na_2SO_4, and then concentrated by distillation to give 34 mg of IIa which was recrystallized from EtOH–H_2O, mp 156—158 °C. The green solid A was dispersed in aqueous EtOH and oxidized with $K_3Fe(CN)_6$. Work-up of the resulting solution by the procedure similar to that described above gave 35 mg of I and 15 mg of IIa.

Irradiation of I in Acidified Methanol. A mixture of I (100 mg, 0.56 mmol) and *p*-toluenesulfonic acid monohydrate

(1 g, 5.3 mmol) in dry MeOH (50 ml) was placed in a quartz vessel, and N_2 was bubbled for 20 min. After irradiation for 7 hr under N_2, $K_3Fe(CN)_6$ in H_2O was added until the solution turned into yellow. The solution was evaporated to dryness under reduced pressure. The residue was neutralized with 5% Na_2CO_3 and then extracted with ether. The extract was dried over Na_2SO_4, and the ether was removed by distillation The residue was chromatographed on alumina. Elution with benzene yielded 65 mg (65%) of unchanged I. Elution with benzene-EtOH (10: 1) yielded 30 mg (26%) of IIb, which was recrystallized from EtOH-H_2O to give the analytical sample, mp 166—167.5 °C.

I (100 mg, 0.56 mmol) in dry MeOH (50 ml) containing 0.1 M HCl was also irradiated for 7 hr under air. Similar work-up of the reaction mixture gave 57 mg (57%) of I and 37 mg (32%) of IIb.

Irradiation of I in Acidified Ethanol. A mixture of I (100 mg, 0.56 mmol) and *p*-toluenesulfonic acid monohydrate (1 g, 5.3 mmol) in dry EtOH (50 ml) was irradiated under N_2 for 7 hr. Work-up of the reaction mixture by the method similar to that described above gave 70 mg (70%) of I and 20 mg (16%) of 1-ethoxyphenazine (IIc) which was recrystallized from EtOH–H_2O to give the analytical sample, mp 126—127 °C (lit,[16] mp 130 °C); picrate, mp 188—190 °C (lit,[16] mp 195 °C). Found: C, 75.10; H, 5.32; N, 12.57%. Calcd for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.38; N, 12.49%.

Irradiation of I in Acidified 2-Propanol. A mixture of I (100 mg, 0.56 mmol) and *p*-toluenesulfonic acid monohydrate (2 g, 10.6 mmol) in dry i-PrOH (100 ml) was irradiated under N_2 for 7 hr. Work-up of the reaction mixture similar to that described above gave 82 mg (82%) of I and 5 mg (4%) of 1-isopropoxyphenazine (IId) which was recrystallized from EtOH–H_2O to give the analytical sample, mp 83—85 °C; NMR (CCl_4) δ 1.58 (d, 6H, J=6 Hz, -CH_3), 4.70—5.30 (m, 1H, $\rangle$CH), 7.72—8.58 (m, 7H, aromatic H); mass spectrum (80 eV) *m/e* 238, 223, 196, 180, 168. Found: C, 75.42; H, 5.70; N, 11.56%. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76.

Irradiation of I in Acetic Acid. A mixture of I (100 mg, 0.56 mmol) and *p*-toluenesulfonic acid monohydrate (1 g, 5.3 mmol) in dry AcOH (50 ml) was irradiated under N_2 for 7 hr. After irradiation, $FeCl_3$ was added to the reaction mixture until the solution turned into yellow. The solution was then evaporated to dryness under reduced pressure, and an aqueous Na_2CO_3 was added to the residue until the neutralized solution was obtained. The neutralized solution was extracted with ether. After the ether extracts were dried over Na_2SO_4, the ether was removed by distillation. The residue was subjected to tlc (silica gel, DMF: AcOH: H_2O= 10: 1: 1). The upper spot was extracted with $CHCl_3$, then the solvent was evaporated to dryness. IR and NMR spectra of the residue were identical with those of the authentic sample of IIe. Quantitative analyses of I and IIe were performed by converting IIe to IIa by treatment with an aqueous NaOH: the residue obtained upon irradiation was dissolved in a mixture of EtOH (5 ml) and 10% NaOH solution (5 ml), and the mixture was kept at 40 °C for 1 hr. A 10% NaOH solution (20 ml) was added to the mixture, and the alkaline solution thus obtained was extracted with ether. Work-up of the ether and aqueous layers gave 75 mg (75%) of I and 20 mg (19%) of IIa.

Irradiation of IIa in 2 M H_3PO_4 Solution. IIa (100 mg, 0.51 mmol) in aqueous 2 M H_3PO_4 (80 ml) was irradiated under air for 7 hr. The solution was neutralized with Na_2CO_3 and extracted with ether. Work-up of the ether extracts resulted in a quantitative recovery of IIa.

Quantum Yield Determinations. A 5 ml of reactant solution was degassed under vacuum by four freeze-pump-thaw cycles in a side arm through which a 1 cm quartz cell was connected. Then the quartz cell and the side arm were closed under vacuum and the solution was transfered into the quartz cell. The absorption spectrum of the reactant solution was recorded, and irradiation was then started. During the course of the photoreactions, additional complete spectra (6—8 times) were taken. Optical densities at 380 nm band of the reactant and at 430 nm band of the product were monitored and the simultaneous equations were used to determine the amount of product formed. A plot of the amount of the product formed *vs.* total quanta absorbed was prepared, and the quantum yield was determined from the slope of the straight line. The photoreaction was never carried out beyond the point where 20% of I has been photolyzed. All studies were made at room temperature. After the photoreaction was ceased, the solution was oxidized by exposing it to air, and the analysis of IIa or IIb was performed by taking absorption spectrum.

A Toshiba SHL-100 UV high-pressure mercury lamp was used as a light source. Light was filtered through a Toshiba UV 31 filter glass. The filter glass permitted to pass the light with the following wavelength distribution: 3% 3130 Å, 18% 3660 Å, 16% 4045 Å, 28% 4358 Å, 28% 5461 Å, 6% 5780 Å. Potassium ferrioxalate actinometer[8] was used for measuring the light intensity. Reproducible output rates of 8.7×10^{16} quanta min^{-1} were recorded.

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