The Photoreduction of Phenazine in Acidic Methanol[1]

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Abstract: The photoreduction of phenazine in strongly and weakly acidic methanol has been studied. In weakly acidic methanol the reaction sequence probably involves protonation of the lowest excited n,π* singlet state followed by electron transfer to produce the "semiquinone" radical PH*, $k_9 \geq 10^7$ sec^{-1}. The PH· radical reacts with solvent to produce dihydrophenazine with $k_{10} = 120$ sec^{-1}. The triplet state of phenazine has a pK_a approximately equal to that of acetic acid in methanol. The rate constant for the decay of the protonated triplet is $k_5 = 1.5 \times 10^3$ sec^{-1} and the unprotonated triplet is $k_3 = 2.6 \times 10^4$ sec^{-1}. The protonated triplet is quenched by dibromomethane, $k_q = 4.7 \times 10^8$ sec^{-1}, and *via* a second-order quenching process, $k_6 = 2 \times 10^9$ M^{-1} sec^{-1}. The intersystem crossing rate for phenazine has been estimated to be $k_2 \geq 10^9$ sec^{-1}. The protonated phenazine triplet is not photoreactive in the media studied. In strongly acidic methanol the reaction sequence is protonation of the lowest n,π* singlet state of the phenazinium cation, PH^+, and electron transfer to produce 5,10-dihydrophenazine, PH_2, $k_{17} = 1.4 \times 10^6$ sec^{-1}. PH_2 reacts with PH^+ to produce a dimer, $k_{18} = 9.5 \times 10^8$ M^{-1} sec^{-1}, which dissociates into two PH· radicals, $k_{19} = 6.0 \times 10^4$ sec^{-1}, which are subsequently protonated to yield a stable radical, $PH_2\cdot^+$.

The electronic spectra of phenazine have been studied by Goodman and Harrel[2a] who determined that the lowest n,π* singlet state lies at 22,989 cm^{-1} in isopentane. Hochstrasser[2b] has suggested the existence of two low-lying n,π* singlet states in phenazine, $^1A_{1g}$ and $^1B_{1u}$, with transitions between $^1A_{1g}$ and the ground state forbidden by symmetry but transitions between $^1B_{1u}$ and the ground state allowed. The lowest energy π,π* singlet state was observed at 27,700 cm^{-1} by Loustauneau, *et al.*[3] The triplet states of phenazine were studied by Goodman and Harrel who assigned a π,π* configuration to the lowest triplet state observed at 15,500 cm^{-1} by Lewis and Kasha[4] and Loustauneau, *et al.*[3] Lewis and Kasha[5] also observed the lowest S → T absorption band of phenazine at 18,000 cm^{-1}. Recently Clark and Hochstrasser[6] have reported the energy of the ^{3}(π,π*) state at 15,448 cm^{-1} using phenazine crystals at 4°K. The energy level of the ^{3}(n,π*) state has never been observed, but was calculated to lie between 18,900 and 20,800 cm^{-1}.[2a]

The electronic spectra of the phenazinium ion have received little attention; Perkampus[7] noted a red shift of the lowest energy π,π* absorption band on protonation. Buettner classified the lowest singlet state as an n,π* state for qualitative reasons.[8]

The photochemistry of phenazine has been studied by Toromanoff,[9] who photolyzed concentrated solutions in alcoholic solvents. He reported the formation of violet, blue, and colorless crystals at various stages of photolysis. He showed that these crystals were solid molecular complexes of phenazine and 5,10-dihydrophenazine of varying stoichiometry. Buettner[8] studied the photochemistry of phenazine and acridine in benzene and water by flash photolysis. He postulated that the lowest triplet state was photoactive for both compounds. Kellman[10] and Kellman and DuBois[11] also studied the photoreduction of acridine and concluded that reaction did not occur from the lowest triplet state, but that the reactive state was ^{3}(n,π*). Subsequently Vander Donckt and Porter[12] showed reasons why the ^{3}(n,π*) assignment was wrong, and established the ^{1}(n,π*) state as the reactive state.

The present investigation is a study of the photochemistry of phenazine in weakly and strongly acidic media. In weakly acidic media (acetate buffers in methanol) dihydrophenazine is the photoreduction product; evidence clearly indicates that the lowest n,π* singlet state is photoreactive. In strongly acidic media (HCl in methanol) the photoreduction product is the green phenazinium radical cation; evidence also indicates that the lowest singlet state is photoreactive. The mechanisms of photoreduction in both media, based on evidence from flash photolysis studies, will be discussed.

Experimental Section

Chemicals. All inorganic and common organic chemicals were of reagent quality or higher and unless otherwise noted were used without further purification.

Sodium pivalate was made by neutralizing pivalic acid to pH 8 with reagent grade NaOH and evaporating the solution to dryness. The white powder obtained was used without further purification.

Phenazine (Aldrich Chemical Co.) was purified by vacuum sublimation followed by recrystallization from hot methanol. Analysis by tlc on Eastman fluorescent chromatographic sheet 6060 using $CHCl_3$ as eluent showed the presence of only one spot, mp 174.9–175.6° uncor (lit.[13] mp 171°).

Instrumentation. A General Electric A-H6 high-pressure mercury arc fitted with a quartz water jacket (George Gates Co., Forest Hills, N. Y.) was used as the light source for quantum yield measurements. A Beckman Model DU monochromator was used to select the photolysis wavelength. The slits on the monochromator were used in the fully open position (*ca.* 2 mm).

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[1] This work was supported in part through funds provided by the U. S. Atomic Energy Commission under Contract AT(30-1)-905.

[2] (a) L. Goodman and R. Harrel, *J. Chem. Phys.*, 30, 1131 (1959); (b) R. M. Hochstrasser, *ibid.*, 36, 1808 (1962).

[3] P. Loustauneau, G. Nouchi, and A. Rousset, *C. R. Acad. Sci., Paris*, 257, 2928 (1963).

[4] G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, 66, 2100 (1944).

[5] G. N. Lewis and M. Kasha, *ibid.*, 67, 994 (1945).

[6] R. H. Clark and R. M. Hochstrasser, *J. Chem. Phys.*, 47, 1915 (1967).

[7] H. H. Perkampus, *Z. Phys. Chem.* (Frankfurt am Main), 6, 18 (1956).

[8] A. V. Buettner, Ph.D. Thesis, University of Minnesota, 1962.

[9] E. Toromanoff, *Ann. Chim.* (Paris), 1, 115 (1956).

[10] A. Kellman, *J. Chim. Phys.*, 63, 936 (1966).

[11] A. Kellman and J. T. DuBois, *J. Chem. Phys.*, 42, 2518 (1965).

[12] E. Vander Donckt and G. Porter, *ibid.*, 46, 1173 (1967).

[13] "Handbook of Chemistry and Physics," 42nd ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960–1961.

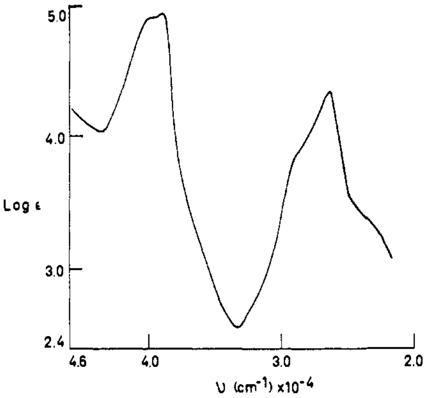

Figure 1. Absorption spectrum of phenazine in methanol, 0.1 M in HCl; the species present is PH^+.

The flash photolysis unit has been described in detail elsewhere.[14] The main flash tubes were powered by a Xenon Corp. (Watertown, Mass.) Model A power supply. In our system this unit was used to provide 500 J of electrical energy to each of two flash tubes (Xenon Corp. FPA-5-10 kV). The $1/e$ time of the flash was 16 μsec with a total base width of *ca.* 40 μsec.

Complete spectra of flash produced intermediates were taken on a Hilger 1.5-m Littrow spectrograph equipped with glass optics, using Eastman Kodak 103a-F plates. A Xenon Corp. Model B spectrographic flash power supply powered the spectral flash source (Xenon Corp. Suntron-3-1/2-7.5 kV). The spectral flash was triggered by a Xenon Corp. Model S spectroscopic delay system.

Kinetics of flash-excited intermediates were followed using a PEK Labs (Palo Alto, Calif.) X-76 xenon arc lamp powered by automobile storage batteries with a dropping resistor to regulate the lamp current. A Bausch and Lomb 500-mm $f/4.5$ grating monochromator with a 600-lines/mm grating was used to select the monitoring wavelength and an RCA 1P21 photomultiplier was used as a detector. The photocurrent from the photomultiplier was fed directly to a log converter constructed from operational amplifiers. The rise time of the log converter was 4 μsec at a reference input current of 30 μA. The log amplifier gave an output of 1 V for an absorbance change of unity. The noise level of the amplifier photomultiplier combination was about 3-5 mV. Characteristic absorbance changes measured were in the range 0.05-0.20. A Tektronix Model 564 oscilloscope with 2A63 and 3B3 plug-ins was used to display the kinetic data which were photographed on Polaroid film. Absorption spectra were taken on a Cary Model 14 spectrophotometer.

Procedures. Quantum yields were measured by pipetting a known amount of a phenazine stock solution into the photolysis cell and evaporating the solvent under vacuum. The solvent system to be used for photolysis was vacuum degassed in a side arm by six freeze-pump-thaw cycles. Then the cell and side arm were sealed off under vacuum and the solvent was mixed with the phenazine until it dissolved. Then the photolysis cell was filled and it and the absorption cell were sealed off. A uv spectrum was obtained and photolysis begun. Six to eight times during the course of the photolysis additional complete spectra were taken. Photolysis was never carried beyond the point where 25% of the phenazine had been photolyzed. Except in the case of strongly acidic solutions, a plot of remaining phenazine *vs.* total quanta absorbed was prepared and the quantum yield was determined from the slope of the line. In the case of the strongly acidic solutions, the product absorbed on the long wavelength side of the reactant. Simultaneous equations were used to determine the amount of product formed. No correction was necessary for product absorption at the photolysis wavelength. The source intensity was measured using the potassium ferrioxalate actimometer.[14b] Actimometer cells were run before, after, and several times during a photolysis to ensure that lamp intensity remained constant during the experiment.

Solutions used in flash photolysis experiments were prepared and degassed immediately before use. Argon was admitted to the flash photolysis cell to a pressure of *ca.* 650 mm before flashing to prevent the formation of solvent bubbles caused by the flash. All flash photolysis solutions were thermostated at 24.9° by circulating water through a jacket surrounding the quartz cell.

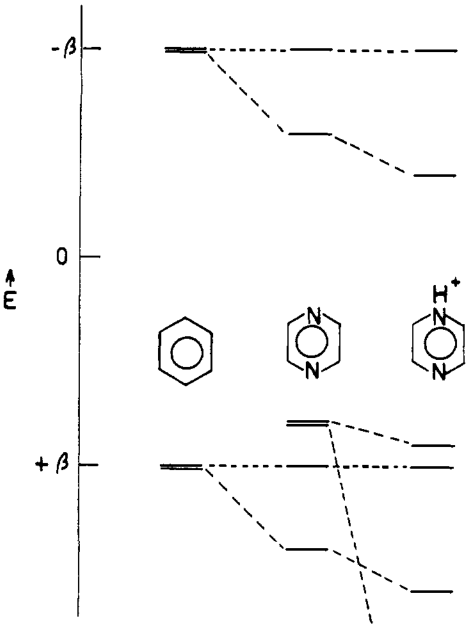

Figure 2. Energy levels of the highest bonding and lowest antibonding HMO's of benzene, pyrazine, and pyrazinium ion.

Results and Discussion

Electronic States. Figure 1 shows the ultraviolet absorption spectrum of monoprotonated phenazine (PH^+). Energy level diagrams for the highest energy π orbitals and lowest energy π^* orbitals for benzene, pyrazine, and pyrazinium ion are shown in Figure 2. The energy levels were calculated by first-order perturbation theory using benzene MO's as base orbitals and Mason's perturbation parameters.[15] These calculations indicate that the red shift on protonation is caused mainly by lowering of the energy of the lowest π^* orbital. This indicates that the lowest energy transition in the pyrazinium ion, and by analogy in PH^+, is still an $n \rightarrow \pi^*$ transition as suggested by the appearance of a long wavelength shoulder in the spectrum of pyrazine in 4 N sulfuric acid.[16] A lowest energy $n \rightarrow \pi^*$ transition is consistent with the observation that solutions of phenazine in acid are nonfluorescent.[8] Figure 2 also indicates the n,π^* transition in PH^+ should be more difficult to observe than in phenazine, because the n,π^* and π,π^* energies should be closer together. Also, in acidic solution, solvation of the unprotonated nitrogen nonbonding electron pair would be increased.

The pK_a^* of the lowest excited singlet state of phenazine can be calculated[17] from the pK_a of the ground state and the spectra of the basic and acidic forms by means of a Förster cycle. The pK_a of the ground state in methanol was determined to be 4.5 by titration, and, coupled with a spectral shift of $-3700\ cm^{-1}$ on protonation, predicts that $pK_a^* \sim 7.5$. A similar but larger shift in the second pK_a^* of phenazine is expected from the magnitude of the spectral shift observed in concentrated sulfuric acid. These calculations indicate that

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[14] (a) D. N. Bailey, Ph.D. Thesis, M.I.T., 1968; (b) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956); C. A. Parker, *ibid.*, **A220**, 104 (1953); J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966.

[15] S. F. Mason, *J. Chem. Soc.*, 1253 (1959).

[16] S. F. Mason, *ibid.*, 1240 (1959).

[17] H. H. Jaffe, H. L. Jones, and M. Isaks, *J. Amer. Chem. Soc.*, **86**, 2932 (1964).

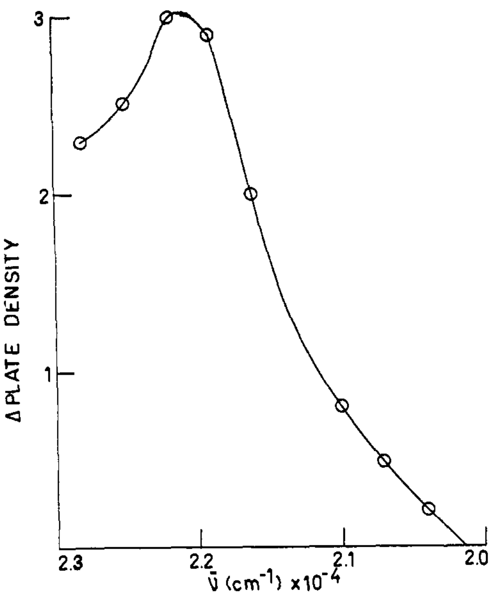


Figure 3. Triplet-triplet absorption spectrum of the protonated phenazine triplet, ${}^3PH^+$: solvent, methanol containing 0.1 *M* acetic acid and 0.1 *M* sodium acetate; phenazine 2.12×10^{-5} *M*. The time delay between main flash bank and spectral flash was 60 μsec. Δ plate density is the change in plate density observed between a spectrum of the spectral flash lamp through only solvent and buffers and through solvent, buffer, and phenazine (Kodak 103a-F plates).

excited-state protonation must be considered when discussing the photochemistry of phenazine in protonic media such as buffered methanol or water.

Photochemistry in Acetate Buffers. The mechanism given by reactions 1–11 is proposed for the photoreduction of phenazine in methanol containing acetic acid–sodium acetate buffers

$$P + h\nu \xrightarrow{k_1} {}^1P^* \quad \text{(excitation)} \tag{1}$$

$${}^1P^* \xrightarrow{k_2} {}^3P \quad \text{(intersystem crossing)} \tag{2}$$

$${}^3P^* \xrightarrow{k_3} P \quad \text{(radiationless deactivation of the lowest triplet)} \tag{3}$$

$${}^3P^* + H^+ \rightleftharpoons {}^3PH^{+*} \quad \text{(triplet protonation)} \tag{4}$$

$${}^3PH^{+*} \rightleftharpoons P + H^+ \quad \text{(radiationless deactivation of the protonated triplet)} \tag{5}$$

$${}^3PH^{+*} + {}^3PH^{+*} \rightleftharpoons 2P + 2H^+ \quad \text{(triplet-triplet annihilation)} \tag{6}$$

$${}^1P^* \xrightarrow{k_7} P \quad \text{(radiationless deactivation of the lowest excited singlet)} \tag{7}$$

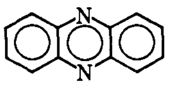
$${}^1P^* + H^+ \rightleftharpoons {}^1PH^{+*} \quad \text{(excited singlet protonation)} \tag{8}$$

$${}^1PH^{+*} + RH \xrightarrow{k_9} PH\cdot + RH^+ \quad \text{(electron abstraction)} \tag{9}$$

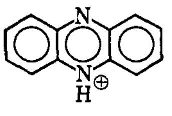
$$PH\cdot + RH \xrightarrow{k_{10}} PH_2 + R\cdot \quad \text{(hydrogen abstraction)} \tag{10}$$

$$2PH\cdot \xrightarrow{k_{11}} PH_2 + P \quad \text{(radical disproportionation)} \tag{11}$$

where P = ground-state phenazine



PH^+ = monoprotonated phenazine



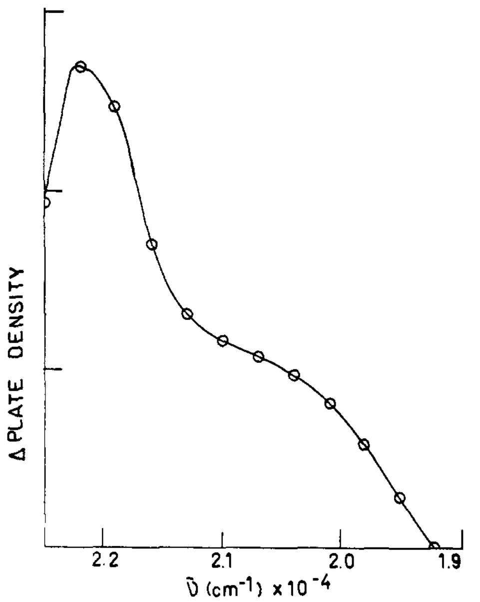
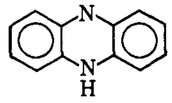
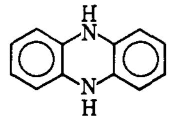


Figure 4. Absorption spectrum of phenazine "semiquinone" radical, PH·: solvent, methanol containing 0.1 *M* acetic acid and 0.1 *M* sodium acetate; phenazine, 2.12×10^{-5} *M*. The time delay between main flash bank and spectral flash was 1 msec. Δ plate density has the same description as Figure 3.

PH· = phenazine semiquinone radical



and PH_2 = 5,10-dihydrophenazine



Complete spectra of flash excited solutions of phenazine in methanol containing acetate buffers showed the presence of two intermediates. The first of these intermediates was short lived (τ = *ca.* 50 μsec) and had a narrow absorption band centered in the 460-mμ region as shown in Figure 3. The second intermediate was longer lived (τ = *ca.* 1 msec) with an absorption band peaking near 460 mμ but extending toward longer wavelengths than the short-lived intermediate, as shown in Figure 4. The short-lived intermediate was identified as the phenazine triplet from the following considerations. Table I indicates that the rate constant for decay is of the same order of magnitude as rate constants previously observed for most triplets in fluid solution.[18] This short-lived intermediate was the only one observed when Freon was used as a solvent, as indicated in Table II. No photoreduction was observed in Freon. The short-lived intermediate was quenched by dibromomethane with a rate constant $k_q = 4.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. On the basis of earlier spectroscopic work[2a,3-6] it may be assumed that the intermediate responsible for the spectrum shown in Figure 3 is for a π,π^* triplet.

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(18) (a) H. Linschitz, C. Steel, and J. A. Bell, *J. Phys. Chem.*, **66**, 2574 (1962); (b) Y. Matsunaga and C. A. McDowell, *Can. J. Chem.*, 38, 1167 (1960); (c) G. Porter and M. W. Windsor, *Proc. Roy. Soc.* (London), **A245**, 238 (1958).

Table I. Rate Constants for Decay of Phenazine Triplet

Solvent	Buffer	Phenazine concn, $M \times 10^6$	$k_{\text{triplet}} \times 10^{-3}$,[a] sec^{-1}	$k_6/\epsilon_t l \times 10^{-4}$,[b] sec^{-1}
MeOH		2.12	26 ± 4	
EtOH		2.12	24 ± 2	
i-PrOH		2.12	23 ± 2	
Freon		1.0	14 ± 4	
MeOH	0.1 *M* HAc, 0.1 *M* NaAc, 0.1 *M* NaCl	2.00	1.1 ± 0.2	2.8 ± 1.0
MeOH	0.1 *M* HAc, 0.1 *M* NaAc	2.12	2.9 ± 0.3	6.7 ± 1.5
MeOH	0.1 *M* HAc, 0.02 *M* NaAc	2.12	1.3 ± 0.3	1.1 ± 1.0
MeOH	0.02 *M* HAc, 0.1 *M* NaAc	2.12	22 ± 4	
MeOH	0.1 *M* HTmAc, 0 1 *M* NaTmAc	2.12	16 ± 2	

[a] In neutral media and when $\text{pH} > \text{p}K_{\text{HAc}} + 0.3$ this corresponds to the rate for deactivation of the unprotonated triplet, k_3. In media where $\text{pH} < \text{p}K_{\text{HAc}} + 0.3$ it is for decay of the protonated triplet, k_5. [b] ϵ_t = molar extinction coefficient of triplet at 460 mμ.

Table II. Rate Constants for Decay of Phenazine "Semiquinone" Radical

Solvent	Buffer	Phenazine concn, $M \times 10^6$	$k_{10} \times 10^{-2}$, sec^{-1}	$k_{11}/\epsilon_r l \times 10^4$,[b] sec^{-1}	ΔA^0 [c]	Flash no.
MeOH		2.12	1.2 ± 0.5	3.0 ± 0.5	0.02 ± 0.01	1
MeOH		2.12			0.07 ± 0.01	2
EtOH		2.12	0.62 ± 0.2		0.02 ± 0.01	1
Freon		2.12			0.00 ± 0.01	1
MeOH	0.1 *M* HAc, 0.1 *M* NaAc, 0.1 *M* NaCl	2.00	1.8 ± 0.6		0.03 ± 0.01	1
MeOH	0.1 *M* HAc, 0.1 *M* NaAc	2.12	1.2 ± 0.4		0.06 ± 0.01	1
MeOH	0.1 *M* HAc, 0.02 *M* NaAc	2.12	1.6 ± 0.4		0.15 ± 0.02	1
MeOH	0.02 *M* HAc, 0.1 *M* NaAc	2.12			0.05 ± 0.01	1
MeOH	0.1 *M* HTmAc,[a] 0.1 *M* NaTmAc	2.12	1.2 ± 0.4		0.11 ± 0.02	1

[a] HTmAc is pivalic acid; NaTmAc is sodium pivalate. [b] ϵ_r = molar extinction coefficient of radical at 460 mμ. [c] ΔA^0 is the initial change in absorbance due to radical. It was determined by extrapolation of the long-lived component of the decay curve at 460 mμ to $t = 0$. Resolution of the two components was easy because of the large difference in decay rates between the triplet, *ca.* 10^3 sec, and the radical, *ca.* 10^2 sec.

The data of Table I indicate that the rate constant for decay of the phenazine triplet is pH dependent. This effect is attributed to protonation of the triplet in sufficiently acidic media. A study of the triplet decay rate as a function of pH in acetate buffers indicated that the pK_a of the phenazine triplet in methanol is close to that of acetic acid, $\text{p}K_a \sim \text{p}K_{\text{HAc}} + 0.3$. This implies that the phenazine triplet is more basic than the ground state, which is consistent with observations for other triplets.[19]

In unbuffered alcohol or in buffered solutions with $\text{pH} > \text{p}K_{\text{HAc}} + 0.3$ the observed decay curve is for the unprotonated triplet, ^3P, having $k_3 = 2.6 \times 10^4\ \text{sec}^{-1}$. In buffers with $\text{pH} < \text{p}K_{\text{HAc}} + 0.3$ the decay curves observed are for the protonated triplet, $^3\text{PH}^+$, with $k_5 = 1.5 \times 10^3\ \text{sec}^{-1}$. In acidic media a second-order component was observed for $^3\text{PH}^+$ decay curves which was attributed to triplet–triplet annihilation. Because the spectral characteristics of ^3P and $^3\text{PH}^+$ seemed to differ only slightly, we used Buettner's value of 5.8×10^3 for the extinction coefficient of $^3\text{PH}^+$ at 460 mμ and our value of $k_6/\epsilon_t l$ from Table I to give $k_6 = 2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$. This value for k_6 implies a diffusion-controlled process which is consistent with triplet–triplet annihilation.

The multiplicity of the photoreactive state of phenazine was established from quenching and quantum yield studies. Flash photolysis studies in phenazine, in 1:1 acetic acid–sodium acetate buffers in methanol, indicated that the triplet, $^3\text{PH}^+$, was efficiently quenched by dibromomethane with a quenching constant, $k_q = 4.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. It was also observed that addition of dibromomethane to phenazine solutions had relatively little effect on the photochemical quantum yield: $\phi = 0.011 \pm 0.002$ for phenazine in methanol with acetic acid–acetate buffer, and $\phi = 0.009 \pm 0.002$ for a similar phenazine solution containing 1 *M* dibromomethane. If $^3\text{PH}^+$ were photoreactive the observed k_q would require a quantum yield of *ca.* 10^{-8} in 1 *M* dibromomethane, *i.e.*, complete quenching of the photochemical reaction. These observations clearly establish the lowest singlet state of PH^+ as the photoreactive state. Excited singlet state reactions have been observed for compounds such as duroquinone[20] and have been proposed in the photoreduction of acridine.[12,21] Hydrogen abstraction would be more likely to occur from an n,π* singlet state of phenazine with its more electron-deficient nitrogen atom than from the relatively electron-rich nitrogen atom of the lowest π,π* triplet state.

The small discrepancy between the two quantum yields observed above probably results from an enhancement of intersystem crossing, between the lowest singlet and the triplet manifold, by the presence of dibromomethane. However, it might be argued that

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(19) (a) J. S. Brinen, D. D. Rosebrook, and R. C. Hirt, *J. Phys. Chem.*, **67**, 2651 (1963); (b) G. Jackson and G. Porter, *Proc. Roy. Soc.* (London), **A260**, 13, (1961).

(20) (a) N. K. Bridge and G. Porter, *ibid.*, **A244**, 259 (1958); (b) *ibid.*, **A244**, 276 (1958).

(21) (a) A. Kira, V. Ikeda, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **39**, 1673 (1966); (b) F. Wilkinson, private communication.

the difference in quantum yields is evidence for two photoreactive states in protonated phenazine, *i.e.*, 82% of the reaction resulting from the lowest singlet state and 18% from the lowest triplet. The difference is not sufficiently precise to warrant such a conclusion; *i.e.*, $\Delta\phi = 0.002 \pm 0.002$. As a check on these data, the relative quantum yield in buffered methanol was determined as a function of dibromomethane concentration. A "Stern–Volmer" plot of the data showed no effect on the relative quantum yield over the range of 0.3–1.0 *M* dibromomethane. Also, if the triplet state were involved in the photochemical reaction to any significant extent, the shape of the kinetic curve observed for the phenazine "semiquinone" radical in flash photolysis studies should reflect this. Since analysis of decay curves at 460 mμ gave two "clean" first-order components, production of $PH\cdot$ from $^3PH^+$ is unlikely. Further evidence against triplet participation in the photoreaction comes from the observation that there was no significant decrease in the amount of $PH\cdot$ produced when 1 *M* dibromomethane was added to phenazine solutions.

Rate constants for intersystem crossing and electron abstraction can be estimated from the extinction coefficient of the $n \rightarrow \pi^*$ transition and the photochemical quantum yield. The $n \rightarrow \pi^*$ transition appears as only a slight shoulder on the long wavelength side of the π,π^* band, making estimation of its extinction coefficient difficult. However, an estimate of $\epsilon \sim 200$ M^{-1} cm^{-1} seems reasonable both from the position of the inflection in the spectrum and from the known extinction coefficients of the monocyclic azines.[16] A value of $\epsilon \sim 200$ leads to an intrinsic excited state lifetime of *ca.* 5×10^{-7} sec[22] or an intrinsic rate constant for fluorescence of $k_f \sim 1.4 \times 10^6$ sec^{-1}. Since no fluorescence was observed from phenazine, other pathways of singlet state deactivation must be at least 10^3 faster. If direct radiationless deactivation of the singlet to the ground state can be neglected,[22] intersystem crossing must proceed with $k_2 \geq 10^9$ sec^{-1}. Electron abstraction must then proceed with a pseudo-first-order rate constant $k_9 \geq 10^7$ sec^{-1} to account for the *ca.* 1% photochemical quantum yield.

Photoreduction of phenazine produces a long-lived species which has been tentatively identified as the phenazine "semiquinone" radical, $PH\cdot$. The first- and second-order rate constants of the radical k_{10} and k_{11} in various solvents are summarized in Table II. The radical undergoes a hydrogen abstraction reaction with a rate constant, $k_{10} = 120$ sec^{-1}, which is independent of the pH of the solution. There is some indication of a second-order component in the decay of the radical which would indicate a parallel disproportionation reaction having a rate constant $k_{11}/\epsilon_r l = 3 \times 10^4$ sec^{-1}. However, since measurement of k_{11} is very dependent on the degree of curvature of the log *A vs. t* plots at short times, and because it was not possible to eliminate the absorption of the triplet which can also cause rounding at short times, the extent of the second-order process could not be established with much reliability.

The data of Table II show a much higher extrapolated yield of $PH\cdot$ radicals for a single flash when buffer was present than for unbuffered alcohols. No decrease in $PH\cdot$ yield occurred when a pivalate buffer was used, implying that electron abstraction, eq 9, does not occur from the methyl group of the acetic acid–acetate buffer.[10,23] This observation helps to establish that $^1PH^{+*}$ is the photoreactive state in buffered methanol as opposed to $^1P^*$. Such a postulate is reasonable, assuming hydrogen abstraction from an alcohol occurs as a two-step process, with electron abstraction being the primary step. Electrochemical studies indicate[14] that PH^+ is more easily reduced than P in the ground state and, to a first approximation, the relative ease of reduction should be similar for excited states.

The sharply increased radical yield observed on repeated flashing of phenazine solutions in unbuffered alcohol is evidence of another reaction, *viz.*, $PH_2 + {}^3P \rightarrow 2PH\cdot$. This reaction was also observed by Buettner, who found it to be diffusion controlled.[8] Buettner found evidence that the addition of PH_2 to phenazine solutions quenches the triplet lifetime, indicating that the triplet is the reactive species. Recently Niizuma, *et al.*,[24] have presented evidence for a similar reaction between acridine and acridan which they also attribute to the lowest triplet $^3(\pi,\pi^*)$ of acridine. Our data did not permit a quantitative evaluation of this reaction because of the very low concentrations of PH_2 present during the experiments. Calculations[14] have shown that the rate of the reaction would have to be faster than diffusion controlled to make any appreciable difference in the decay rate of the triplet even after half of the phenazine was converted to dihydrophenazine.

Photochemistry in Strongly Acidic Solutions. The mechanism given by reactions 12–20 is proposed for photoreduction of phenazine in strongly acidic solutions

$$PH^+ \xrightarrow{h\nu} {}^1PH^{+*} \qquad \text{(excitation)} \tag{12}$$

$$^1PH^{+*} \xrightarrow{k_{13}} {}^3PH^{+*} \qquad \text{(intersystem crossing)} \tag{13}$$

$$^3PH^{+*} \xrightarrow{k_{14}} PH^+ \qquad \text{(radiationless deactivation of the protonated triplet)} \tag{14}$$

$$PH^{+*} + H^+ \rightleftarrows {}^1PH_2{}^{2+*} \qquad \text{(excited state protonation)} \tag{15}$$

$$^1PH_2{}^{2+*} \xrightarrow{k_{16}} PH^+ + H^+ \qquad \text{(radiationless deactivation)} \tag{16}$$

$$^1PH_2{}^{2+*} + RH_2 \xrightarrow{k_{17}} PH_2 + RH_2{}^{2+} \qquad \text{(photoreaction)} \tag{17}$$

$$PH_2 + PH^+ \xrightarrow{k_{18}} (PH)_2 + H^+ \qquad \text{(complex formation)} \tag{18}$$

$$(PH_2) \xrightarrow{k_{19}} 2PH\cdot \qquad \text{(dissociation into radicals)} \tag{19}$$

$$PH\cdot + H^+ \xrightarrow{k_{20}} PH_2{}^+ \qquad \text{(radical protonation)} \tag{20}$$

where all the symbols are the same as those for the mechanism of photoreduction in buffered methanol except $^1PH_2{}^{+*}$ = doubly protonated excited phenazine singlet, $(PH)_2$ = association complex of phenazine and dihydrophenazine, and $PH_2\cdot^+$ = protonated "semiquinone" radical.

The photoreduction of phenazine in methanol containing 0.1 *M* strong acid proceeds to a stable green

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[22] E. Lim, quoted in R. E. Kellogg and R. G. Bennett, *J. Chem. Phys.*, **41**, 3042 (1964).

[23] (a) C. F. Wells, *Nature*, **177**, 483 (1956); (b) C. F. Wells, *Trans. Faraday Soc.*, **57**, 1703 (1961); (c) *ibid.*, **57**, 1719 (1961).

[24] S. Niizuma, Y. Ikeda, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **40**, 2249 (1967).

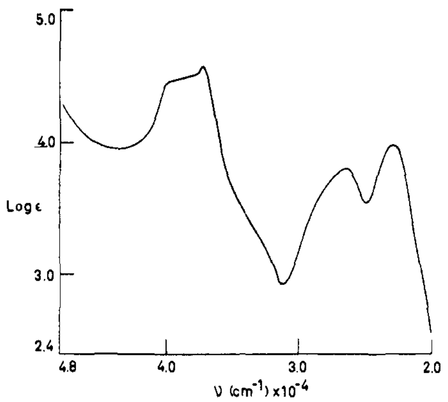

Figure 5. Absorption spectrum of phenazine radical ion, $PH_2\cdot^+$: solvent, 0.1 M HCl in methanol.

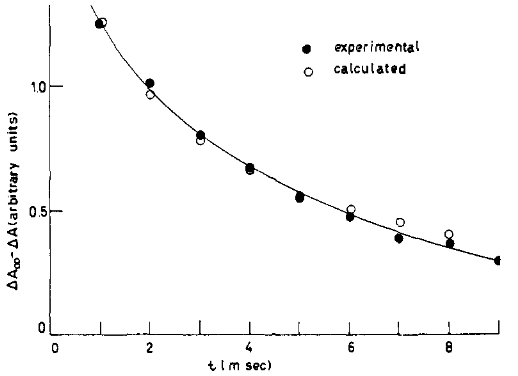

Figure 6. Simulated and experimental kinetic curves for 8.48 × 10^{-7} M phenazine in methanol: 0.05 M in sulfuric acid; λ 445 mμ.

species having the electronic absorption spectrum shown in Figure 5. The green species was identified as the $PH_2\cdot^+$ radical by comparison of its esr spectrum with the known esr spectrum of $PH_2\cdot^+$ previously reported.[18b,25] The quantum yield for production of $PH_2\cdot^+$ was 0.094 ± 0.003 in 0.1–1 M HCl in methanol.

No transient absorption was observed in the visible spectrum of flash-excited phenazinium ion solutions in methanol except for absorption in the 445-mμ region due to the growth of the $PH_2\cdot^+$ radical. Because no photochemically inert solvent could be found in which phenazine hydrochloride was sufficiently soluble, it was not possible to observe transients under conditions where no photoreduction occurred.

Initial kinetic results on solutions 2.12 × 10^{-5} M in phenazine indicated that the growth of the $PH_2\cdot^+$ radical was first order with a rate constant of *ca.* 4 × 10^3 sec^{-1}. The growth rate was independent of acid concentration in the 0.1–1 M region. Because the magnitude of the rate constant seemed consistent with reaction from a triplet state, oxygen quenching of the reaction was studied and a rate constant of 4.2 × 10^5 M^{-1} sec^{-1} was observed. Also, 10^{-2} M dibromomethane had essentially no effect on the kinetics of $PH_2\cdot^+$ formation. The small quenching constant for oxygen and lack of quenching by dibromomethane indicate that a triplet state is not involved in the photoreduction of phenazine in strongly acidic media.

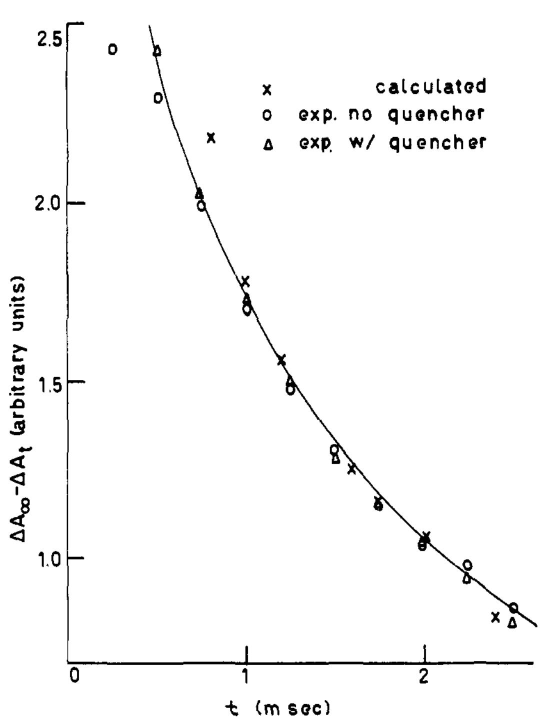

Figure 7. Simulated and experimental kinetic curves for 1.27 × 10^{-5} M phenazine in methanol: 0.05 M in sulfuric acid; λ 445 mμ.

When the phenazine concentration was decreased, the kinetics for production of $PH_2\cdot^+$ took on second-order characteristics. At 8.48 × 10^{-7} M phenazine, a rate constant of $k/\Delta\epsilon l \sim 4 \times 10^3$ sec^{-1} was observed. A $\Delta\epsilon$ of 7 × 10^3 M^{-1} cm^{-1} was determined from the absorption spectra for the difference in extinction coefficients of PH^+ and $PH_2\cdot^+$ at 445 mμ; the absolute rate constant was then calculated to be 4 × 10^8 M^{-1} sec^{-1}. The reaction sequence which seemed to fit best the observed kinetic data was a second-order reaction followed by a first-order reaction, as indicated by eq 18 and 19 in the proposed mechanism.

Using the above model, kinetic curves were simulated on an IBM 360 computer using a generalized kinetics program.[26] Initially 50% phenazine reduction was assumed and trial rate constants were chosen for k_{18} and k_{19}. The trial rate constants were varied until the concentration–time profile for concentrations of 8.48 × 10^{-7} M and 1.27 × 10^{-5} M phenazine. The best match for the curves was obtained using rate constants $k_{18} = 9.5 \times 10^8$ M^{-1} sec^{-1} and $k_{19} = 6.0 \times 10^4$ sec^{-1} as shown in Figures 6 and 7.

The kinetic data presented are consistent with a one-step reduction of phenazine to dihydrophenazine and subsequent reaction with PH^+ to produce a complex, $(PH)_2$, which then dissociates into two $PH\cdot$ radicals, that are subsequently protonated, *viz.* eq 17–20. A similar mechanism has been proposed recently for the photoreduction of benzophenone in strong basic solution.[27] The formation of complexes between phenazine and dihydrophenazine has been observed to occur in the solid state by Toromanoff.[9] Fellion and

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(25) (a) J. R. Boulton, A. Corrington, and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 465 (1962); (b) K. H. Hausser, A. Häbich, and V. Franzen, *Z. Naturforsch.*, **16a**, 836 (1961); (c) Y. Matsunaga and C. A. McDowell, *Proc. Chem. Soc.*, 175 (1960).

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(27) (a) G. A. Russel and E. J. Geels, *Tetrahedron Lett.*, 1333 (1963); (b) F. Wilkinson, private communication.

Uebersfeld[28] produced the green $PH_2\cdot^+$ radical by adding an acidified solution of phenazine to a solution of dihydrophenazine in a reaction that is probably mechanistically similar to the one proposed here. Unfortunately they gave no kinetic data. If the complex were a N—H···N bonded complex, for instance, hydrogen bonding could stabilize it until it split by homolytic cleavage to give two neutral PH· radicals. These neutral radicals would then be rapidly protonated by the high concentration of free protons in the medium.

In Figure 7, the computer-simulated curve or 1.27×10^{-5} M phenazine solutions matches the experimental curve for $t > 750$ μsec but not for $t < 750$ μsec. The mismatch at $t < 750$ μsec has been shown to be partially due to the presence of another shorter lived species absorbing at 445 mμ. The PH^+ triplet is known to absorb in this region and has a lifetime consistent with the mismatch of the curves. The addition of 10^{-2} M dibromomethane to the reaction mixture caused the experimental curve to show none of the rounding associated with the unquenched data and to match more closely the simulated curve, as shown in Figure 7. The remaining mismatch between the curves has been ascribed to the initial assumptions that half of the phenazine present initially is in each of the reactive forms [(PH_2) and (PH^+)]. This would cause an error in the absolute magnitude of the second-order rate constants which would not be greater than a factor of 4 or 5.

Rate constants for eq 13 and 17 may be estimated in the manner used previously. Again assuming $\epsilon = 200$ M^{-1} cm^{-1} for the $n \rightarrow \pi^*$ transition buried under the π,π^* band, $k_{13} \geq 10^9$ sec^{-1} and $k_{17} \geq 10^8$ sec^{-1}. The computer model was changed to include the possible effect of eq 17 on the growth rate of $PH_2\cdot^+$. It was found that pseudo-first-order rate constants larger than 10^7 sec^{-1} had no effect on the over-all rate of reaction when $k_{18} = 9.5 \times 10^8$ M^{-1} sec^{-1} and $k_{19} = 6.0 \times 10^4$ sec^{-1}.

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Intramolecular Perturbation Effects in Diamine–Iodine Charge–Transfer Complexes[1]

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Abstract: A method has been developed for determining the association constants (K_1 and K_2) of the 1:1 and 2:1 iodine complexes of diamines in nonpolar solution. The method was checked with triethylamine which, as expected, gave $K_2 = 0$ within experimental error and a value of K_1 which is in good agreement with values obtained by the Benesi–Hildebrand procedure. With all the polyfunctional amines studied $K_1 > K_2$, or in the limit, $K_1 \simeq K_2$. Compounds of the type $(CH_3)_2N(CH_2)_nN(CH_3)_2$ gave little indication of interaction between the nitrogen atoms, and the trend in K_1 values can be interpreted in terms of steric effects. With $n = 6$, $K_1 \simeq K_2$. The cage amines quinuclidine (ABCO) and triethylenediamine (DABCO) emerge as the strongest donors reported to date, with K_1 values of 3.3×10^5 and 6.8×10^4 l./mol, respectively, at 23°, and $K_1/K_2 \simeq 30$ for DABCO. Only the comparison of these compounds furnishes clear-cut spectral and thermodynamic evidence of interaction between the donor sites. By contrast, hexamethylenetetramine behaves like a simple trialkylamine with a diminished number of alkyl groups. For this tetramine, $K_1/K_2 \simeq 5$. The spectral features of the amines and their iodine complexes and the nature of the perturbation effects are discussed.

Of the known n–σ types of charge-transfer complexes, those involving iodine and amines as acceptor and donors, respectively, have been most extensively studied. In these complexes the intermolecular bond is localized, and the N–I–I moiety is linear.[2] For ammonia and monofunctional amines, the complexes are strong with formation constants in the range 10^2–10^4 l./mol (20°) and enthalpies between −5 and −12 kcal/mol.[3] They are also quite polar (*e.g.*, the dipole moment of the triethylamine–iodine complex is *ca.* 5.5 D[4]), which is the indicative of substantial charge transfer in the ground state. In the interpretation of spectral and thermodynamic data, it is generally assumed that only 1:1 complexes are formed, and these properties pertain to adducts of this stoichiometry. There is some evidence that, under certain conditions, complexes

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[1] This research was supported by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contracts No. AF 19(628)-3836 and F 19628-67-C-0118.

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