Photochemistry of Phenoxazine. A Flash-Photolytic Study[1]

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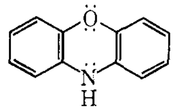
Abstract: The flash photolysis of phenoxazine has been studied in several solvents. Three transient species have been identified. These are the first triplet state (λ_{max} 465 nm), the neutral radical resulting from loss of the nitrogen-bonded hydrogen atom (λ_{max} 370 nm), and the corresponding cation radical (λ_{max} 535 nm). The kinetic behavior of these species has been delineated. The results are consistent with the formation of the cation radical by a biphotonic process involving the triplet state. In the presence of oxygen, neither the triplet state nor the cation radical is observed. Continuous monochromatic irradiation experiments indicate that peroxides are probably formed which, on further photolysis, produce 3-phenoxazone as the stable oxidation product.

Phenoxazine (PH, I) and its derivatives have, for some time, been known to undergo oxidation and reduction reactions and to show complex photochemical and photobiological properties. Detailed knowledge of the photochemical behavior of these compounds is of interest not only because of their close relationship to numerous dyes, but also because of the significant pharmacological activity shown by several representatives.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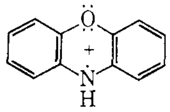
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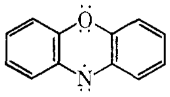
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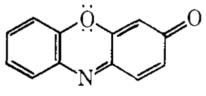
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The pioneering work by Michaelis and coworkers[2] demonstrated that, in strongly acidic solution, phenoxazine undergoes a one-electron oxidation to the corresponding cation radical ($PH\cdot^+$, II). A photochemical investigation of phenoxazine and some related compounds by Lewis and Bigeleisen,[3] which utilized a continuous irradiation technique in rigid medium, established that the radical cation II as well as the corresponding neutral radical ($P\cdot$, III) are generated. These authors proposed that $PH\cdot^+$ is produced simply by primary photolytic electron ejection, and that the radical $P\cdot$ arises from the radical cation by loss of a proton; *i.e.*, $PH \rightarrow PH\cdot^+ + e^- \rightarrow P\cdot + H^+$. Two recent electron spin resonance studies have confirmed that solutions of phenoxazine in sulfuric acid contain $PH\cdot^+$.[4] Moreover, by the same technique Tsujino[5] has shown that the neutral radical $P\cdot$ is formed from phenoxazine in a mixture of dimethyl sulfoxide and acetic anhydride, and that it reacts further to produce dimers.

The spectroscopy of phenoxazine has also received some recent attention. Thus a study of the emission and absorption properties of this compound has shown that the first two transitions in the singlet manifold are polarized perpendicularly to each other, and that the polarization of the phosphoresence parallels that of the fluorescence.[6] Further, an electron spin resonance study of the phosphorescent triplet state of phenoxazine, performed with mixed crystals as well as in rigid glass matrices, suggests that it arises from a $\pi \rightarrow \pi^*$ electronic transition and that it is a B_2 state (C_{2v} symmetry).[7]

While there have been several investigations of the photochemistry of phenothiazine, to our knowledge the only reference to the photochemical behavior of phenoxazine is in the early paper of Lewis and Bigeleisen.[3] We have therefore undertaken a detailed study of the photochemistry of this compound using primarily the technique of flash photolysis. It was a specific aim of the work reported in this paper to identify the transient species generated, and to delineate their interrelationships and kinetic behavior.

Experimental Section

Materials. Phenoxazine (Aldrich Chemical Co.) was purified by sublimation and recrystallization from aqueous ethanol under a nitrogen atmosphere. The material used had mp 156.5°. The spectral quality solvents, ethanol (U. S. Industrial Chemicals Co.), benzene, methylcyclohexane (Matheson Coleman and Bell), and *n*-heptane (Fisher Scientific Co.), were tested for interfering impurities and found suitable for use without further purification. Methyl methacrylate (Eastman Organic Chemicals) was freed from inhibitor by the method of Unterleitner and Hormats.[8]

Apparatus and Procedure. Spectral measurements were made with a Beckman DK-1 recording spectrophotometer. The two types of flash apparatus which were used in this study are described in more detail elsewhere, and here only a summary of their specifications is given. Unit 1[9] is an apparatus of conventional geometry which is based on four xenon-filled flash tubes. With the total input energy of 900 J used in this work, the flash duration (1/e time) is *ca.* 10 μsec. The detection system consists of a continuous

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[1] (a) This research was supported by HEW Public Health Service Grants No. 5 R01 RH00302 and 9 R01 ES00376, and by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under Contract No. F19628-67-C-0118; (b) presented in part at the Fifth International Conference on Photochemistry, Yorktown Heights, N. Y., Sept 2–5, 1969.

[2] L. Michaelis, S. Granick, and M. P. Schubert, *J. Amer. Chem. Soc.*, **63,** 351 (1941).

[3] G. N. Lewis and J. Bigeleisen, *ibid.*, **65,** 2419 (1943).

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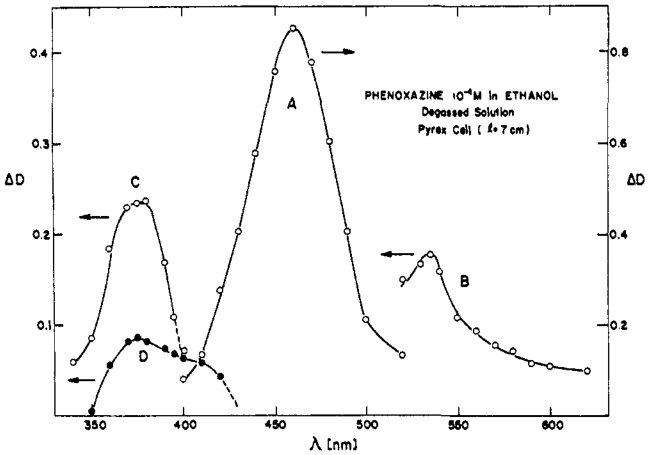

Figure 1. Transient absorption in the 340-370-nm region. The times after flash excitation are *ca.* 20 μsec for spectra A, B, and C, and *ca.* 2 msec for spectrum D.

analyzing beam (450-W stabilized xenon arc lamp) which is monitored by means of a Jarrell-Ash *f*/6.3 grating spectrograph fitted with an EMI 9558AQ photomultiplier tube and a Tektronix Type 535-A oscilloscope. Unit 2 has a geometry which permits broadside illumination and is particularly suited for small samples and low-temperature studies.[10] With input energies in the range used in this study (20–200 J), the light output (quanta cm^{-2}/flash) of the flash tube (Novatron-609, Xenon, Inc.) varies linearly with the electrical energy, and the flash duration is *ca.* 10 μsec. With this unit, the analyzing beam is provided by a 108-W projection lamp (GE CG-121-AX1) and the detection assembly consists of a Bausch & Lomb 100-mm, *f*/3.5 monochromator and an EMI 9514S photomultiplier tube.

Digitization of the oscilloscope records is accomplished by means of a Gerber digital data reduction system (Model GDDRS-3B) which is coupled to an IBM 026 keypunch. A computer program is used to calculate the change in optical density as a function of time and to provide least-squares fits with first-order, second-order, or mixed first- and second-order kinetic expressions according to an iterative, nonlinear regression procedure.

Solutions for the flash experiments were extensively outgassed by repetitive freeze–pump–thaw cycles in special vessels[11] designed to provide multiple fillings of the "Pyrex" flash cell (diameter 2.0 cm, path length 7.0 cm for unit 1 and 1.5 cm for unit 2). To prevent bubble formation, the solutions were finally placed under a 1-atm pressure of argon. Monochromatic continuous irradiation experiments were performed with light provided by a 150-W medium-pressure mercury arc lamp and Bausch & Lomb 100-mm *f*/3.5 monochromator.

The apparatus for the measurement of emission spectra and yields[12] consists of a 450-W xenon arc excitation source which is used in conjunction with a Bausch & Lomb 500-mm *f*/4.4 monochromator and a Spex 750-mm *f*/6.8 analyzing spectrophotometer. Provision is made for the accurate temperature control of the samples to 77°K, which are irradiated at right-angle to the direction of emission measurement, and for correction of the spectra for the response characteristics of the instrument. Quinine bisulfate in aqueous 0.1 *N* sulfuric acid was used as the standard substance (ϕ_f = 0.55[13]).

Results

Transient Spectra and Kinetics. (a) In Ethanol. The first absorption band of phenoxazine has λ_{max} *ca.* 320 nm (ϵ ~8000) in all the solvents examined. In the flash experiments, excitation was confined to this band. The transient spectrum in ethanol at room temperature is shown in Figure 1. Immediately after the flash (~20 μsec), the dominant species is A (λ_{max} 465 nm) which decays according to a first-order kinetic law (k_1 = (2.30 ± 0.20) × 10^4 sec^{-1}, $\tau \approx$ 44 μsec). We have assigned this transient as the first triplet state on the basis of the following arguments. (1) Henry and Kasha[14] have reported that a transient species with λ_{max} 460 nm is generated by the continuous irradiation of phenoxazine in 3-methylpentane glass at 77°K, which they assigned as the triplet state. (2) The same transient absorption appears in solid poly(methyl methacrylate) at 90°K. In this medium, the lifetime of the species is 2.0 sec, which matches exactly the phosphorescence lifetime under identical conditions.

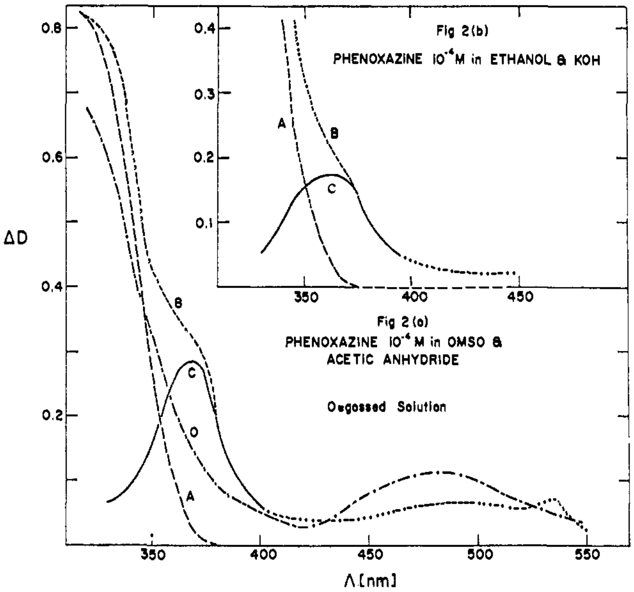

Figure 2. (a) Spectral changes in the solution of phenoxazine in dimethyl sulfoxide–acetic anhydride: curve A, initial absorption of phenoxazine; curve B, after 2 hr; curve C, difference between curves A and B; curve D, *ca.* 20 hr after mixing. (b) Spectral changes in the solution of phenoxazine in ethanol containing potassium hydroxide: curve A, absorption of phenoxazine in ethanol; curve B, after addition of potassium hydroxide; curve C, difference between curves A and B.

The spectrum taken immediately after the flash also shows bands with maxima at *ca.* 535 nm (B) and 365 nm (C). Band B corresponds with the absorption spectrum of the phenoxazine cation radical PH·$^+$, which is reported[2] to have λ_{max} 530 nm. Owing to a slight overlap with the tail portion of the triplet–triplet absorption, the kinetic order of the decay of this species could not be unequivocally established. However, the decay is approximately first order with $k_1 \approx$ 1.7 × 10^4 sec^{-1} ($\tau \approx$ 60 μsec.). Absorption band C decays in *ca.* 500 μsec and leaves band D with λ_{max} 365 and 415 nm. We assign the absorption C to the neutral phenoxazine radical P· (III) for the following reason. Two methods have been reported for the chemical generation of this radical. In one method, phenoxazine is merely dissolved in a mixture of dimethyl sulfoxide and acetic anhydride.[5] We have followed this reaction spectroscopically with the results shown in Figure 2a. Curve A represents the initial absorption, which was measured immediately after dissolving the phenoxazine in the thoroughly outgassed solvent mixture. After about 2

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[10] J. R. Huber, R. P. Widman, and K. Weiss, *Rev. Sci. Instrum.*, **40**, 1103 (1969).

[11] W. M. Moreau, T. A. Tyler, and K. Weiss, *J. Chem. Educ.*, **43**, 435 (1966).

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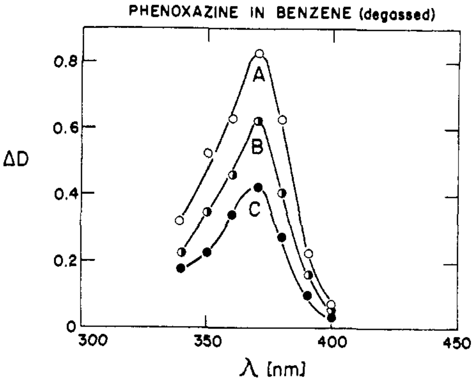

Figure 3. Transient absorption in the 300–400-nm region in benzene: A, 40 μsec after flash; B, 1.8 msec after flash; C, absorption remaining after decay.

hr a pronounced shoulder appears (curve B). The difference between curves A and B is shown as curve C, which has λ_{max} 365 nm. After 20 hr, curve C has been transformed into curve D. The growth and decay of band C corresponds closely with the growth and disappearance of the esr signal due to radical II. We have also made a spectral study of the behavior of phenoxazine in ethanol containing potassium hydroxide which, according to Heineken and coworkers,[15] produces the neutral radicals of a series of oxazine dyes. The results are shown in Figure 2b. *Immediately* after mixing curve B is obtained which, when the original absorption (curve A) is subtracted, provides curve C with λ_{max} 365 nm. The coincidence of the spectra produced by these two methods with the flash-produced spectrum is taken as evidence for the production of the neutral radical P· by photolysis.

The neutral radical (Figure 1, curve C) decays with approximative second-order kinetics ($k_2/\epsilon_{app}(370)$ = $(2.30 \pm 0.50) \times 10^5$ cm sec^{-1}, where ϵ_{app} is the apparent extinction coefficient. The species D (Figure 1), which decays much more slowly with first-order kinetics (k_1 = 1.5 ± 0.2 sec^{-1}, $\tau \approx 0.66$ sec), remains as yet unidentified.

When a solution of phenoxazine in ethanol which is 0.1 *M* in hydrogen chloride is flashed, the quantity of triplet state produced is comparable to that in neutral solution. However, no absorption due to the neutral radical is observed; instead, approximately twice the amount of cation radical $PH\cdot^+$ is produced.

(b) In Benzene. The results in benzene are qualitatively similar to those in ethanol (*cf.* Figure 3, where only the 300–400-nm region is shown). Significant differences are: (1) the cation radical $PH\cdot^+$ (λ_{max} 535 nm) remains for several days in this solvent, embuing the solution with a pink color; (2) the initially produced absorption (curve A, Figure 3), which is presumed to be due to the neutral radical, decays in *ca.* 500 μsec ($k_2/\epsilon_{app}(370) \approx 2 \times 10^5$ cm sec^{-1}). This rapid decay leaves curve B, which disappears more slowly to curve C. The latter absorption appears to be stable indefinitely; the species responsible for it has not been identified.

(c) In Heptane and Methylcyclohexane. In both of these solvents, the transient spectra and kinetic behavior are quite similar to those observed in benzene, with the exception that the cation radical $PH\cdot^-$ decays rapidly, as is the case in ethanol.

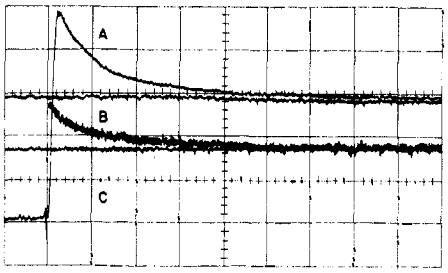

Figure 4. Oscilloscope traces at 370 nm in heptane. Time base for A is 200 μsec/cm and for B, 0.5 sec/cm. Curve C represents the absorption remaining after decay.

The kinetic behavior at 370 nm in heptane, which is entirely analogous to that in benzene and in methylcyclohexane, is shown in Figure 4. The decay of the radical (curve A) has a rate constant $k_2/\epsilon_{app}(370)$ = $(4.6 \pm 0.6) \times 10^5$ cm sec^{-1} in heptane and $k_2/\epsilon_{app}(370)$ = $(2.8 \pm 0.5) \times 10^5$ cm sec^{-1} in methylcyclohexane. Curve B shows the decay of the remaining species (*cf.* curve, B, Figure 3) which follows first-order kinetics and corresponds to a lifetime of about 1 sec. As in the case of benzene, the final absorption (curve C) seems to be stable.

The relative initial concentrations of the various transient species and the observed triplet lifetimes are summarized in Table I.

Table I. Triplet Lifetimes and Relative Initial Concentration of Transients

	Initial Changes in OD due to			Triplet
Solvent	P· (370 nm)[a]	$PH\cdot^+$ (535 nm)	Triplet (465 nm)	lifetime, μsec
Ethanol	0.23	0.15	0.81	44
Benzene	0.85	0.08	0.29	26
Methylcyclohexane	0.35	0.04	0.25	32
Hexane	0.33	0.04	0.25	26

[a] These values are based on the assumption that the initial change in optical density at 370 nm is entirely due to the radical. If the species responsible for the absorption remaining after the initial rapid decay are assumed to be produced during the flash, the density values for the solvents in the order given are 0.23, 0.45, 0.24, and 0.24.

(d) Effect of Oxygen. The behavior in the presence of oxygen was examined in all of the above solvents. In no case was absorption due to the triplet state and the cation radical observed. Only in benzene does there appear to be immediate formation of the radical in greatly diminished amount, which then disappears very rapidly. In ethanol, heptane, and methylcyclohexane solution there is, instead, a growth of absorption in the 370-nm region which remains without decay.

Products of Photolysis in Air. The course of the reaction in methylcyclohexane and in ethanol in the presence of air was examined by continuous photolysis of 10^{-4} *M* solutions of phenoxazine at 313 nm. After *ca.* 1 hr new absorption appears near 370 nm (*cf.* Figure 5). Further irradiation with 365-nm light caused this band to disappear and a new band to appear with λ_{max} 440 nm in methylcyclohexane and λ_{max} 450 nm in ethanol. This absorption coincides with that reported for the phenoxazone IV.[16] The infrared

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(15) F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.*, **37**, 1479 (1962).

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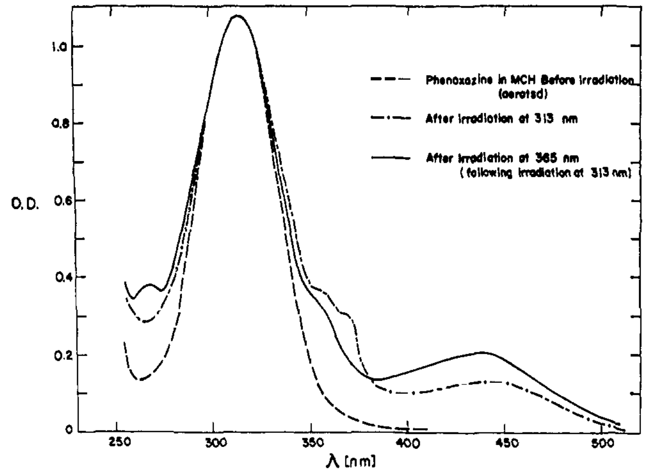

Figure 5. Photolysis of phenoxazine in aerated methylcyclohexane solution.

spectrum, in carbon tetrachloride, of the solid residue obtained by evaporation of the solvent shows the infrared bands in the 1400–1700-cm^{-1} region which have been reported for compound IV.[17]

Fluorescence Measurements. The results of fluorescence quantum yield measurements in solution at room temperature are listed in Table II. The quantum yields obtained with 350-nm excitation in benzene and in methylcyclohexane are seen to be significantly higher than those obtained with excitation at 320 nm in all three solvents and at 350 nm in ethanol. These values are apparently distorted by the formation of a highly fluorescent photolysis product in these two solvents, which absorbs in the excitation region. This is borne out by measurements of the excitation spectra, which implicate a substance with λ_{max} ~360 nm.

Table II. Fluorescence Quantum Yields

Solvent	Quantum yield[a] 320 nm[b]	Quantum yield[a] 350 nm[b]
Ethanol	0.025	0.026
Benzene	0.025	0.040
Methylcyclohexane	0.031	0.080

[a] At room temperature; estimated error ± 10%. [b] Excitation wavelength.

Discussion

The photochemical excitation of phenoxazine generates at least three transient species. The triplet state has been identified beyond reasonable doubt. Spectral comparison with the chemically generated species lead us to conclude that the transient absorption bands with λ_{max} 370 and 535 nm are due to the neutral radical P· and radical cation PH·$^+$, respectively. The experimental results are consistent with the following scheme, which will form the basis for further discussion.

$$\mathrm{PH} \xrightarrow{h\nu} {}^1_1\mathrm{PH} \qquad (1)$$

$${}^1_1\mathrm{PH} \longrightarrow \mathrm{PH} + h\nu_f \text{ (fluorescence)} \qquad (2)$$

$${}^1_1\mathrm{PH} \longrightarrow {}^3_1\mathrm{PH} \qquad (3)$$

$${}^1_1\mathrm{PH} \longrightarrow \mathrm{P}\cdot + \mathrm{H}\cdot \qquad (4)$$

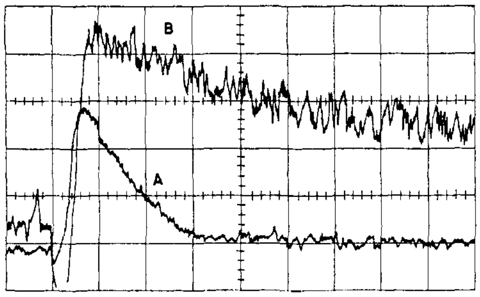

Figure 6. Oscilloscope traces in ethanol: curve A, 460 nm (triplet state); curve B, 360 nm (neutral radical). The time base is 50 μsec/cm for both.

$${}^3_1\mathrm{PH} \longrightarrow \mathrm{PH} + h\nu_p \text{ (phosphorescence)} \qquad (5)$$

$${}^3_1\mathrm{PH} \xrightarrow{h\nu_t} {}^3_n\mathrm{PH} \qquad (6)$$

$${}^3_n\mathrm{PH} \longrightarrow \mathrm{PH}\cdot^+ + e^- \qquad (7)$$

The upper indices designate the multiplicity of the state, and the lower indices the level of excitation (first or higher excited state). For simplicity, these designations are omitted for the singlet ground state of the molecule. The scheme further omits steps such as radiationless processes within the manifold of a given multiplicity, which must inevitably be assumed to occur.

For the production of the radical P· we propose the primary photochemical dissociation given by eq 4. The excited states of certain secondary amines have previously been suggested to dissociate in this manner.[18] In view of the N–H bond strength (*ca.* 80 kcal/mol[19]), the average energy of *ca.* 95 kcal/mol of the exciting light used for the phenoxazine experiments is adequate for bond dissociation. In further support of step 4, it is found that both the neutral radical and triplet state concentrations reach their maxima simultaneously during the flash (Figure 6).[20] Thus the lowest triplet state, which in any case has an energy content of <63 kcal/mol, is not likely to be the precursor of the neutral radical.

The further reaction of the radical P· evidently involves primarily dimerization (eq 8). Dimeric compounds have been isolated from the radical produced by chemical means.[5] Also consistent with this interpretation is the finding that, in benzene, *n*-heptane, and methylcyclohexane, the kinetics of the disappearance of the radical are strictly second order. In ethanol, the kinetic plots leave open the possibility of the participation of a first-order process in the decay, *e.g.*

$$\mathrm{P}\cdot + \mathrm{P}\cdot \longrightarrow \mathrm{P}_2 \qquad (8)$$

$$\mathrm{P}\cdot + \mathrm{RH}_2 \longrightarrow \mathrm{PH} + \mathrm{RH}\cdot \qquad (9)$$

where RH_2 represents the solvent. The only evidence supporting this reaction is the observation that, in ethanol, the permanent disappearance of phenoxazine is less than in the hydrocarbon solvents. With respect

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[17] H. Musso and H. G. Matthies, *Chem. Ber.*, **90**, 1814 (1957).

[18] (a) G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 188 (1952); (b) C. H. Bamford, *ibid.*, 17, (1939).

[19] J. A. Kerr, R. C. Sekhar, and A. F. Trotman-Dickenson, *ibid.*, 3217 (1963); J. A. Kerr, A. F. Trotman-Dickenson, and M. Wolter, *ibid.*, 3584 (1964).

[20] If the radical were *not* to decay, this result by itself would constitute incontroversible proof that the reaction ${}^3P_1 \rightarrow P\cdot + H\cdot$ is not significant. This condition is almost obtained since only *ca.* 10% of the radicals decay during the half-life of the triplet state. Under these circumstances, the maximum radical concentration is expected to be reached measurably beyond the time of the maximum triplet concentration if the latter species is the source of the radical.

to the fate of the hydrogen atoms (eq 4), one can only speculate that they react rapidly with the solvent or with ground-state phenoxazine or recombine to ultimately furnish products of unknown structure.

It is proposed that the cation radical $PH\cdot^+$ is produced by the further photolysis of the first triplet state. That the excitation of a triplet state can give rise to ions has been demonstrated for N,N,N′N′-tetramethyl-*p*-phenylenediamine[21] and for certain acridines.[22] In the present case, our reasons for postulating a biphotonic ionization process involving the triplet state are as follows. (1) The triplet state is implicated because in aerated solutions the production of the radical cation is entirely suppressed. (2) The direct ionization of the first excited singlet state is clearly not possible since the light absorbed in the ground state corresponds to only *ca.* 3.5 eV. The ionization potential of phenoxazine, on the other hand, is expected to lie in the range 6–8 eV.[23] We have obtained a better estimate of this parameter by means of the charge-transfer complexation method.[23a] Thus a solution of phenoxazine and tetracyanoethylene in dichloromethane shows a charge-transfer maximum at 728 nm, which corresponds to a gas-phase ionization potential of 7.0 ± 0.5 eV. Now, the maximum energy content of the first triplet state is *ca.* 2.75 eV,[6] and the triplet–triplet band (*cf.* Figure 1) shows that light absorption by this state can contribute up to *ca.* 3.1 eV to this value. The total energy of the higher triplet state reached by biphotonic excitation is thus about 6 eV, which is still less than 7.0 ± 0.5 eV. However, it has been shown that the energy necessary for ionization is lower in a condensed phase than in the gas phase.[24] (3) Although the ionization cross section of the more energetic singlet state may well exceed that of the triplet state, the longer lifetime of the latter makes it a more probable intermediate for a biphotonic process. The excited singlet-state radiative lifetime has been estimated as *ca.* 8 nsec by evaluation of the absorption and fluorescence spectra,[25] which is to be compared with the triplet lifetime of 26–44 μsec. (*cf.* Table I). (4) The initial amount of radical ion produced increases with the initial concentration of the triplet state in the various solvents (*cf.* Table I).

Weller and coworkers have shown that direct ionization of excited singlet states can occur *via* charge-transfer complexation in the presence of appropriate electron acceptors.[26] In our experiments, only the solvent could act as the acceptor. The absorption spectra of phenoxazine showed no evidence of charge-transfer complex formation in the ground state. Moreover, the constancy of the fluorescence efficiencies with excitation at 320 nm in solvents of different polarity (Table II) indicates that a charge-transfer ionization mode is unlikely to be important for phenoxazine.

Despite painstaking efforts, no spectral evidence for the solvated electron, which is reported to absorb near 700 nm, could be obtained in ethanol. Pulse radiolysis studies indicate that the rate constant $k_{2(\mathrm{EtOH})}$ for the decay of this species is $<10^5\ M^{-1}\ \mathrm{sec}^{-1}$ [27] and, on this basis, should be measurable in our experiments. We can only surmise that the solvated electron, which must be assumed to result from the ionization process, reacts very rapidly with the ground state of phenoxazine.

A second mechanism for the formation of the ion $PH\cdot^+$ seems to be operative in the acidic ethanol solution, where this ion is produced in larger quantity than in a neutral solution and formation of the radical $P\cdot$ is entirely suppressed. Rapid protonation of the radical provides a reasonable explanation for this behavior.

$$P\cdot + H^+ \longrightarrow PH\cdot^+ \qquad (10)$$

Finally, we consider the photolysis in the presence of oxygen, where neither the triplet state nor the cation radical is in evidence. The phenoxazone IV may arise from the decomposition of initially produced peroxides by the reaction sequence

$$P\cdot + O_2 \longrightarrow PO_2\cdot \longrightarrow \text{peroxide} \longrightarrow \text{IV}$$

An alternative or, possibly, concurrent mechanism for the formation of peroxides involves quenching of the phenoxazine triplet state by ground-state molecular oxygen ($^3\Sigma_g^-$) to produce singlet oxygen ($^1\Delta_g$, $^1\Sigma_g^+$). The latter can then react with ground-state phenoxazine and ultimately furnish peroxides.

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