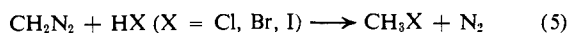


**Table II.**  $\Delta H_f^\circ(\text{CH}_2\text{N}_2)$  and  $D(\text{CH}_2\text{-N}_2)$  Obtained by Various Methods

Process	Method	Threshold energy, eV	$\Delta H_f^\circ(\text{CH}_2\text{N}_2)$		$D(\text{CH}_2\text{-N}_2)$		Remarks
			eV	kcal/mol	eV	kcal/mol	
$\text{CH}_2\text{N}_2 \rightarrow \text{CH}(\text{A}^2\Delta) + \text{H} + \text{N}_2$	Photodissociation	$8.99 \pm 0.05$	$\geq 2.22 \pm 0.05$	$\geq 51.3$	$\leq 1.81 \pm 0.05$	$\leq 41.7 \pm 1$	This work
$\text{CH}_2\text{-N}_2 \rightarrow \text{CH}_2^+ + \text{N}_2$	Electron impact	$12.3 \pm 0.1$ $12.7 \pm 0.3$	$\geq 2.1$ $\geq 1.7$	$\geq 49$ $\geq 40$ $\geq 67$	$\leq 1.9$	$\leq 44$	Ref 3a Ref 4 Ref 6
$\text{CH}_2\text{N}_2 \rightarrow \text{CH}_2 + \text{N}_2$	Pyrolysis			$> 48 + E_1$		$\leq 35$	<i>a</i>
$\text{CH}_2\text{N}_2 + \text{HX} \rightarrow \text{CH}_3\text{X} + \text{N}_2$ (X = Br and I)	Decomposition of $\text{CH}_3\text{X}$			$< 57 + E_1$			

<sup>a</sup>  $E_1$  is the translational and internal energy of  $\text{CH}_3\text{X}$  and  $\text{N}_2$ . See ref 7a.

Another independent estimate of the upper and lower limits for  $\Delta H_f^\circ(\text{CH}_2\text{N}_2)$  comes from the work of Hassler and Setser.<sup>7a</sup> From the observation that  $\text{CH}_3\text{I}$  formed in reaction 5 decomposes while  $\text{CH}_3\text{Br}$  does not, an in-



ternal energy of the activated  $\text{CH}_3\text{X}$  should be above 54 kcal/mol for  $\text{CH}_3\text{I}$  and below 67 kcal/mol for  $\text{CH}_3\text{Br}$ , respectively.  $(48 + E_1) \leq L H_f^\circ(\text{CH}_2\text{N}_2) \leq (57 + E_1)$  kcal/mol, where  $E_1$  is the sum of the energy in various degrees of freedom in  $\text{CH}_3\text{X}$  and in  $\text{N}_2$ . In order to have an agreement with our lower limit of 51.3 kcal/mol,  $E_1 = 3.3$  kcal/mol is obtained, which places an upper limit of 60.3 kcal/mol on  $\Delta H_f^\circ(\text{CH}_2\text{N}_2)$ . Our threshold measurement for the production of  $\text{CN}(\text{B}^2\Sigma)$  from various cyanogen compounds<sup>25</sup> indicates that the experimentally determined threshold, in some cases, is as much as 5 kcal/mol above the minimum energy re-

quired for the reaction, even when a distinct threshold is observed. In the case of  $\text{CH}_2\text{N}_2$ , three products are formed, each of which can carry excess energy in various degrees of freedom. Therefore, it is not unlikely that the observed threshold is several kcal/mol above the minimum energy required, which is within the range of values set by Hassler and Setser. The activation energy for reaction 4 is given by  $\Delta H_f^\circ(\text{CH}_2\text{N}_2) + E_A - \Delta H_f^\circ(\text{CH}_2)$ , where  $E_A$  is the activation energy for the thermal decomposition of  $\text{CH}_2\text{N}_2$ . Adopting the upper limit  $\Delta H_f^\circ(\text{CH}_2\text{N}_2) \leq 60$  kcal/mol,  $E_A = 32$  kcal/mol, and  $\Delta H_f^\circ(\text{CH}_2) = 93$  kcal/mol, almost no activation energy is expected for (4), supporting the observation that the reaction proceeds efficiently even at 20°K.<sup>27,28</sup> A summary of the  $\Delta H_f^\circ(\text{CH}_2\text{N}_2)$  and  $D(\text{CH}_2\text{-N}_2)$  values obtained by various methods appears in Table II.

**Acknowledgment.** Thanks are due to Dr. R. F. Hampson, Jr., for many helpful discussions.

## Flash Spectroscopy and Photoreduction of Phenazine

Steven M. Japar<sup>1</sup> and E. W. Abrahamson\*

*Contribution from the Department of Chemistry,  
Case Western Reserve University, Cleveland, Ohio 44106.  
Received September 28, 1970*

**Abstract:** Flash illumination of methylcyclohexane (MCH) and trifluoroethanol (TFE) solutions of phenazine populates both singlet and triplet excited states. The quantum yield of triplet formation is 0.21 in MCH and 0.30 in TFE. Singlet-state reactions are of little consequence in MCH, but are quite complex in TFE, leading to the formation of primary and secondary reduction products, *i.e.*, the phenazine semiquinone and the phenazine cation radical, respectively. The quantum yield of the cation radical is 0.08, and about 15% of this can be stabilized. The quantum yield of phenazine disappearance is  $\geq 0.04$  and results completely from excited-singlet-state reactions. Evidence is presented for the inclusion of a dimer-forming reaction in the TFE system.

In recent years the flash photolysis of phenazine has received considerable attention. Studies have been carried out in benzene, water,<sup>2</sup> and acid solutions.<sup>3</sup> All the studies have resolved at least two intermediates. In all cases the lowest triplet state, protonated in the acid systems,<sup>3</sup> was detectable through its triplet-triplet absorption spectrum, and its rate of decay was found to vary from about  $2 \times 10^4$  to  $5 \times 10^3$  sec<sup>-1</sup>, depending on

the solvent. In acid solution a long-lived intermediate was also formed, decaying with a rate constant of 120 sec<sup>-1</sup>. Intermediates of this type were also noted in benzene and water,<sup>3</sup> but the yields were so low that little in the way of quantitative data could be obtained. In weak acid and neutral solutions the major product of the photoreduction was dihydrophenazine.<sup>2-4</sup> In strongly acid solutions, however, the samples became lime green and the isolated product was identified as the phenazine cation radical.<sup>3</sup> In all cases the interme-

(1) NSF Trainee, 1965-1966; NASA Trainee, 1966-1969; Division of Physics, National Research Council of Canada, Ottawa, Canada.

(2) A. V. Buettner, Ph.D. Thesis, University of Minnesota, 1962.

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

(4) A. Dufraise, A. Etienne, and E. Tormanoff, *C. R. Acad. Sci.*, **232**, 2379 (1951); **235**, 759 (1952).

diolate generally believed responsible for the photoreduction was a semiquinone. However, Buettner<sup>2</sup> felt that the reaction proceeded *via* the triplet manifold, while Bailey, *et al.*,<sup>3</sup> presented quenching data to indicate that the singlet manifold was responsible.

The present study was designed to clarify the mechanism of the photoreduction of phenazine in strong hydrogen-bonding solvents through identification of the various intermediates produced.

## Experimental Section

**Flash Spectroscopy System.** The flash spectroscopy apparatus has been described in detail elsewhere.<sup>5</sup> Basically, it consisted of two flash lamps connected in series with a hydrogen thyratron, used for triggering. The system operated at 10 kV, with two 1- $\mu$ F Wego high-voltage capacitors. Approximately 50 J of energy was discharged through the flash tubes with a flash half-life on the order of 10  $\mu$ sec.

A beam splitter allowed for recording of data at two different wavelengths simultaneously. The detection system consisted of two Bausch and Lomb 250-mm focal length grating monochromators. The monochromator outputs were fed into RCA 6342-A multiplier phototubes, and the outputs of the latter were fed, *via* an operational amplifier circuit, into two dual-channel Tektronix oscilloscopes, Types 555 and 551. Each oscilloscope was fitted with a Tektronix C-12 trace recording camera.

**Materials.** The methylcyclohexane used was research grade material further purified by washing it with concentrated sulfuric acid and distilled water and passing it twice through a 3-ft basic alumina column. This was followed by distillation and storage over dry calcium oxide.

Analysis of 2,2,2-trifluoroethanol (Aldrich Chemical Co.) by gas-liquid partition chromatography indicated no impurities in quantities greater than 0.03%. The material was used as received.

Phenazine was purified by vacuum sublimation at 10 mm of pressure and subsequent threefold recrystallization from ethanol. The melting point of the purified material, obtained in the form of yellow needles, was 171°.

**Degassing of Samples.** All samples were degassed by slight variation of the simple freeze-thaw process with an apparatus designed for the semiautomatic degassing of large volumes of solvent<sup>6</sup> until the vapor pressure over the frozen solution was less than  $5 \times 10^{-6}$  Torr.

**Temperature Studies.** These studies were carried out with the sample prepared in a 5-cm Pyrex cell equipped with an outer jacket. The sample was cooled or heated by circulating a thermostating solution through the outer jacket. Temperatures could be regulated to  $\pm 0.5^\circ$ .

Temperature measurement was accomplished with a calibrated Fenwall thermistor inserted into the jacketed sample cell.

**Actinometry of Flash-Excited Samples.** The absolute quantum yield of intermediate formation was determined by potassium ferrioxalate actinometry.<sup>7</sup> To match the actinic flash light to the actinometer solution, optical filters consisting of aqueous solutions of cobalt and copper sulfates were used to fill the jacket surrounding the sample cell. The concentrations of the filter, actinometer, and sample solution were adjusted so that the integrated absorbances of the latter two were equal within the bandpass of the filter.<sup>8</sup> This procedure allowed direct measurement of the number of photons of light absorbed by the phenazine sample.

**Rate Data Analysis.** The procedure for taking rate data and the calculation of the decay kinetics has been described.<sup>5,9</sup> The decay kinetics were extrapolated to zero time relative to the flash in order to calculate the maximum absorbance of the intermediate. Since the intermediate's extinction coefficient could be easily calculated from the extent of phenazine bleaching,<sup>5,10</sup> the maximum inter-

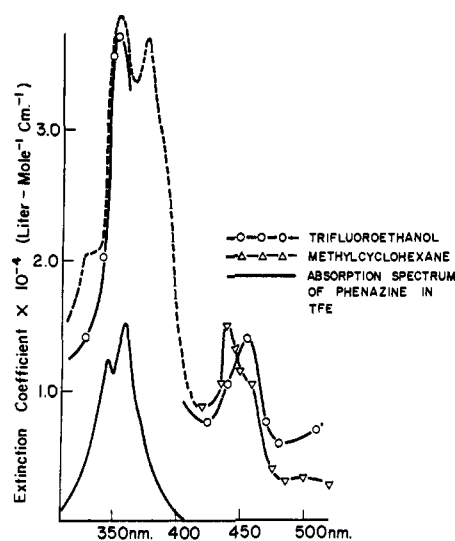


Figure 1. Triplet-state absorption of phenazine in methylcyclohexane and trifluoroethanol. In methylcyclohexane the extinction coefficients in the dotted portion of the spectrum are only imprecisely determined.

mediate concentration and its quantum yield of formation could be calculated.<sup>5,8</sup>

## Results

**Transient Absorption Spectra.** In the initial experiments two different transients were observed. Figure 1 shows the spectrum of one of the transient species in trifluoroethanol (TFE) and methylcyclohexane (MCH). The spectra have been identified as belonging to the lowest triplet state of phenazine (see Discussion). In TFE no absorption can be detected in the region from 360 to 400 nm, presumably because such absorption is masked by bleaching of the ground-state phenazine absorption spectrum (also shown in Figure 1). In MCH small signal levels and difficulty in decay analysis render somewhat imprecise the extinction coefficients at wavelengths shorter than 420 nm. The absorption spectra are seen to be quite similar except for a slight red shift in the low-energy band when the solvent is changed from MCH to TFE.

In both solvents the decay of these spectra, measured at various wavelengths throughout the observed bands, is found to be first order in transient concentration. In MCH ( $2.3 \times 10^{-4}$  M solution) the rate constant is  $2.4 (\pm 0.2) \times 10^4 \text{ sec}^{-1}$ , and is found to be insensitive to temperature ( $-3$  to  $46^\circ$ ) and initial phenazine concentration ( $5.6 \times 10^{-8}$ – $2.3 \times 10^{-4}$  M). Although the decay of the triplet-state absorption spectrum is also first order in TFE, a marked dependence of the first-order rate constant on the initial phenazine concentration is found (Figure 2). The largest decay rate constant,  $1.6 \times 10^4 \text{ sec}^{-1}$ , found at the highest phenazine concentrations, is only about 75% of the constant found in MCH.

The quantum yield of formation of the triplet state was determined by the method of absorbance matching described above. For  $10^{-4}$  M phenazine solutions the quantum yield is  $0.30 \pm 0.05$  in TFE and  $0.21 \pm 0.04$  in MCH.

The second species detected is found only in the flash photolysis of TFE-phenazine solutions. The absorption spectrum of the intermediate is shown in

(5) S. M. Japar, Ph.D. Thesis, Case Western Reserve University, 1969.

(6) J. R. Wiesenfeld and S. M. Japar, *Talanta*, **16**, 619 (1969).

(7) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(8) W. Dawson and E. W. Abrahamson, *J. Phys. Chem.*, **66**, 2542 (1962).

(9) E. W. Abrahamson, R. Adams, and V. J. Wulf, *ibid.*, **63**, 441 (1959).

(10) S. G. Hadley and R. A. Kellar, *ibid.*, **73**, 4351, 4356 (1969).

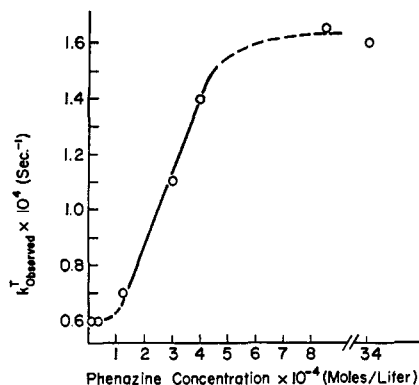


Figure 2. Observed rate constants of triplet-state decay vs. phenazine concentration in trifluoroethanol.

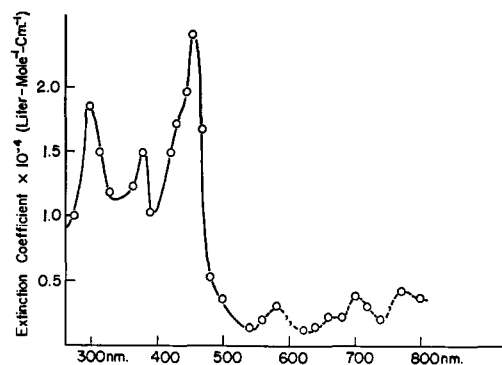
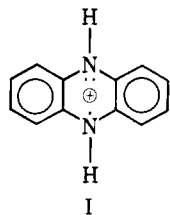


Figure 3. Spectrum of the long-lived intermediate produced in the flash photolysis of phenazine in trifluoroethanol.

Figure 3. The spectrum shows very distinct structure in the 500–800-nm region, where extinction coefficients are uncertain because of the small signals involved. However, the structure is quite reproducible. It will be seen in the Discussion that the species responsible for this spectrum is the dihydrophenazine cation radical I.



Unlike the case of the triplet state, flash oscillograms show that the formation of cation radical occurs during the 150  $\mu$ sec immediately after the photolytic flash. Unfortunately, the kinetics of this formation are not amenable to analysis.

The rate of decay of this intermediate is independent of phenazine concentration over a narrow range ( $2.3 \times 10^{-3}$ – $7.9 \times 10^{-4}$  M), with a first-order decay rate constant of  $19.6 \text{ sec}^{-1}$ . In the course of the decay, however, the oscillogram trace does not return to the base line, thus indicating the formation of some stable species which absorbs in the same wavelength region as the intermediate. If a sample is repeatedly flashed, or irradiated ( $\lambda > 320 \text{ nm}$ ), the sample slowly turns lime green and a spectrum very similar to Figure 3 can be obtained on a recording spectrophotometer. Completely analogous results have been obtained in this laboratory during irradiation of degassed phenazine–isopropyl alcohol solutions.

The quantum yield of formation of the cation radical, determined at 455 nm, is  $0.080 \pm 0.015$  (in a  $1.2 \times 10^{-4}$  M solution). The quantum yield of formation of the stable species, being identical with or very similar to that of the transient cation radical (see Discussion), was determined from actinometry of five successive flashes of a single sample and subsequent measurement, on a Cary 14R spectrophotometer, of the absorption produced at 455 nm. The figure obtained for the quantum yield is  $0.012 \pm 0.003$ .

Under the general conditions outlined above the quantum yield of phenazine disappearance in TFE is at least 0.04. The value is probably a minimum because the majority of products of phenazine photoreduction, primarily dihydrophenazine, absorb at 370 nm, the

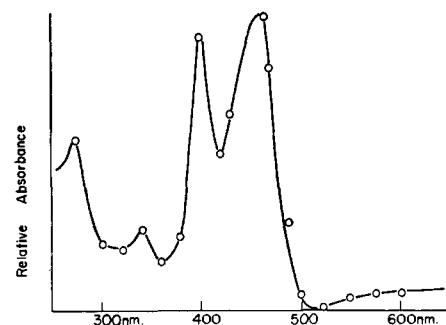


Figure 4. Spectrum of the long-lived intermediate produced in the flash photolysis of phenazine in the presence of the cation radical.

wavelength at which phenazine disappearance was monitored. In MCH the phenazine concentration was affected only after very long irradiation with the full output of a 450-W xenon arc.

Flash photolysis of samples containing large amounts of “stable cation radical” (these samples were prepared by prolonged irradiation of phenazine–TFE solutions) were also attempted. Under these conditions the triplet state is not observed and a relatively long-lived intermediate is formed in apparently low yield. There is also a significant change in the transient absorption spectrum (compare Figures 3 and 4), and the decay rate constant of the new transient species is  $450 \text{ sec}^{-1}$ . Continued flashing produces a decrease in the sample absorbance due to the stable cation radical. Mass spectrographic analysis of the yellow product solution ( $\lambda_{\text{max}}$  355 nm) obtained under the above conditions shows very complex structure from 150 to 360 amu of the kind usually associated with aromatic hydrocarbon systems.

**Quenching Experiments.** In order to delineate the nature of the two transient species, molecular oxygen was used as a quencher. The flash photolysis of a  $3 \times 10^{-4}$  M phenazine–TFE solution in the absence of air yielded a maximum absorbance (average of four experiments) of the short-lived species (the triplet state) of 0.025 at 445 nm. The associated decay rate constant was  $1.11 \times 10^4 \text{ sec}^{-1}$ . On addition of a known amount of air from a side arm (the total pressure in the sample cell was about 2 Torr), the decay rate constant increased to  $1.68 \times 10^4 \text{ sec}^{-1}$ , while the maximum absorbance decreased to 0.009. In both cases the maximum absorbance due to the second species (the cation

radical) was 0.06 at 445 nm. Therefore, marked oxygen quenching of the short-lived species does not affect the formation of the longer lived species.

## Discussion

**The Triplet State.** The assignment of the transient species responsible for the spectra in Figure 1 as the lowest triplet excited state of phenazine is quite straightforward. First, the spectra in Figure 1 agree quite well with those already found for the triplet state in hydrocarbon<sup>2</sup> and polar solvents.<sup>3</sup> Secondly, the observed decay rate constants are in very close agreement with those of Bailey, *et al.*,<sup>3</sup> for both types of solvents. Third, and most important, is the fact that both the yield and decay of the intermediate are drastically affected by the presence of small amounts of oxygen, as would be expected if it were a triplet excited state.

The minor differences in behavior of this intermediate in the two solvents can also be easily explained in terms of triplet excited states. The slight increase in the quantum yield of the intermediate when the solvent is changed from MCH to TFE is probably a manifestation of hydrogen bonding, where the predominant effect may be the shift to higher energies of the  $^1\text{ }^3(\text{n}, \pi^*)$  states on hydrogen bonding, thus bringing them closer in energy to the  $^1(\pi, \pi^*)$  state and enhancing the radiationless probabilities of populating the triplet manifold through increased spin-orbit coupling.<sup>11</sup>

Part of the solvent effect on the decay rate constant can also be explained. In the case of retinal, where the lowest triplet state is  $\pi, \pi^*$  in character, a marked decrease in the decay rate constant was found when the solvent system was changed from "inert" to hydrogen bonding.<sup>8</sup> In that case mixed-solvent studies pointed to the effect arising from a hydrogen-bonded solvent-triplet state complex. Thus, in the case of phenazine, where the lowest triplet state is again  $\pi, \pi^*$  in character,<sup>12</sup> a similar result might be expected, and, indeed, the 25% decrease of the decay rate constant in TFE *vs.* MCH at high phenazine concentrations points to such an effect. Unlike the present case, however, no concentration effects were noted with retinal in pure hydrogen-bonding solvents. As TFE is slightly more acidic than water,<sup>13</sup> it is possible that part of the concentration effect may arise from competition between decaying hydrogen-bonded and protonated triplet states. However, in that case the observed decay should be the sum of the two individual first-order decays. The observed decay traces do not support this hypothesis. Another possibility is a complex between ground- and excited-state phenazine molecules. However, in such a case an analogous effect should be detectable in MCH, which it is not. Considerably more detailed solvent studies are needed to properly resolve all the effects involved.

**Dihydrophenazine Cation Radical.** It has been pointed out that a second intermediate, as well as a stable species, with the spectrum shown in Figure 3, has been found in the photolysis of phenazine in TFE. A similar green product has been reported in the flash photolysis of phenazine in strongly acidic methanol, and the spectrum presented, in the wave-

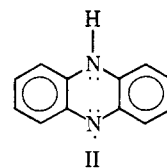
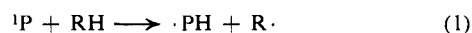
length region shorter than 500 nm,<sup>3</sup> agrees with that shown in Figure 3. The species responsible for the spectrum has been isolated and its esr spectrum was found to be identical with that of the dihydrophenazine cation radical.<sup>3</sup>

In light of the above observations it can be reasonably concluded that the second intermediate observed in TFE, as well as the species responsible for the stable lime-green solution color, is the dihydrophenazine cation radical. If this is the case the quantum yields found for the transient and stable species (0.080 *vs.* 0.012) show that only 15% of the transient cation radical formed during a flash remains unquenched. This would seem to indicate that the observed decay is not due to an inherent instability of the transient cation radical, *i.e.*, an excess of vibrational energy. A possible explanation will be explored in the next section.

**Mechanism of Phenazine Photochemistry.** It is to be expected that photoreduction *via* hydrogen abstraction should proceed directly from the lowest  $^1(\text{n}, \pi^*)$  state of phenazine containing an electrophilic nitrogen atom rather than from the lowest  $^3(\pi, \pi^*)$  state.<sup>14</sup> Various experimental results have verified this point in the present system. The quenching data presented definitely eliminate the lowest  $^3(\pi, \pi^*)$  state from consideration as the electronic excited state responsible for the photoreduction and clearly implicate the singlet manifold in cation-radical production. Similar results have been obtained for the flash photolysis in acetate buffer-methanol solutions and in strong acid-methanol solutions where a marked increase in the rate of triplet-state decay did not affect the quantum yield of photoreduction when dibromomethane was used as a triplet quencher.<sup>3</sup>

Although the above discussion points to the type of excited state responsible for the production of the dihydrophenazine cation radical, it gives little insight into the actual mechanism of cation radical formation.

The radiative lifetime of the lowest  $^1(\text{n}, \pi^*)$  state, uncomplicated by radiationless deactivation, is expected to be on the order of  $10^{-7}$  sec.<sup>15</sup> Therefore, as cation-radical formation proceeds from the singlet manifold at times on the order of 100  $\mu\text{sec}$ , the singlet excited state involved must undergo a preliminary reaction before cation-radical formation takes place. If the  $^1(\text{n}, \pi^*)$  state is involved, the most logical preliminary step is hydrogen abstraction from the solvent to yield a semiquinone (II).



It should be emphasized that in these experiments there is no direct evidence of the semiquinone. Its presence is based on (1) the fact that the cation radical cannot be formed directly from either the  $^1(\text{n}, \pi^*)$  or the  $^3(\pi, \pi^*)$  excited states; (2) the semiquinone is a logical

(11) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).

(12) R. H. Clark and R. M. Hochstrasser, *ibid.*, **47**, 1915 (1967).

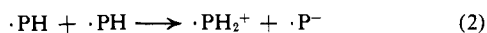
(13) P. Bollinger and F. A. Long, *J. Amer. Chem. Soc.*, **81**, 1050 (1959).

(14) E. W. Abrahamson and I. Panik, *Advan. Mol. Spectrosc., Proc. Int. Meet. 4th*, 1959, **1**, 354 (1962).

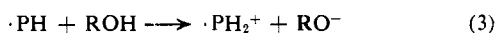
(15) E. C. Lim, quoted in R. E. Kellogg and R. G. Bennett, *J. Chem. Phys.*, **41**, 3042 (1964).

product in such systems. In benzene very slight absorption arising from a second intermediate has been observed as a relatively long-lived low-intensity tail on the excited triplet-state decay, and the source of the absorption is assigned as the semiquinone.<sup>2</sup> Since the spectrum of the semiquinone is reported<sup>3</sup> to strongly overlap the spectra of both the triplet state and cation radical reported here, its relatively short life<sup>3</sup> (and perhaps low extinction coefficient) could result in similar evidence of its presence in TFE being hidden. In fact, if the semiquinone does contribute slightly to absorption in the region where cation-radical formation is monitored, some of the difficulty in the kinetic analysis of the cation-radical formation might be explained.

The semiquinone can yield the cation radical by two possible reactions. The first is a disproportionation



while the second is the abstraction of an acidic hydrogen



Because of the large excess of alcohol, the second reaction, being very similar to the mechanism proposed by Bailey, *et al.*, involving direct protonation of the semiquinone in strongly acidic media,<sup>3</sup> would be expected to predominate. In strong acid the formation of the cation radical is essentially first order,<sup>3</sup> while in the present case the kinetics have not been resolved. However, the time courses of the formation of the cation radical agree quite well. In TFE the formation of the cation radical occurs in the first 150  $\mu\text{sec}$  (corresponding to a "first-order" rate constant of  $\sim 6 \times 10^3 \text{ sec}^{-1}$ ) while the measured rate constant<sup>3</sup> in strong acid is  $4 \times 10^3 \text{ sec}^{-1}$ .

Some spectroscopic evidence, however, suggest the partial applicability of reaction 2. The published spectrum of the cation radical covers the region shown by the solid line in Figure 3. The spectrum of the anion is unknown, but that of the acridine anion radical has been reported<sup>16</sup> to consist of a series of five peaks from 500 to 700 nm, with maximum absorbance at 640 nm. The similarity of that description with the dotted portion of Figure 3 is interesting and suggests that eq 2 may be of some importance.<sup>17</sup>

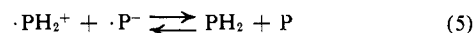
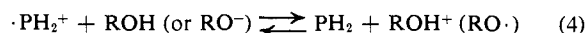
The observed first-order decay of the dihydrophenazine cation radical along with the fact that 15% of the

(16) J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **90**, 6421 (1968).

(17) It should be noted that Zanker and Benicke<sup>15</sup> have produced spectra similar to those in ref 16 during the irradiation of various acridans in deoxygenated ethanol at  $-180^\circ$ . In that instance, however, three distinct species were thought to be responsible, two neutral radicals and the cation radical.

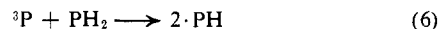
(18) V. Zanker and D. Benicke, *Z. Phys. Chem. (Frankfurt am Main)*, **66**, 34 (1969).

cation radical is stabilized cannot be readily explained. It seems reasonable to ascribe the first-order kinetics to an electron-transfer process involving TFE, or perhaps the anion radical.

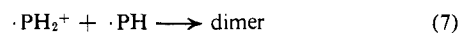


When the polarity of the solvent is considered, and if (4) and/or (5) represent equilibria, the residual stabilization of the cation radical might be explained.

**Photoproduct Chemistry.** The flash photolysis results obtained with samples containing large amounts of stable cation radical cannot be explained in terms of transient absorption belonging to the cation radical since it shows none.<sup>3</sup> It seems reasonable that at least a portion of the spectrum shown in Figure 4 arises from the phenazine semiquinone (see the reported spectrum of the semiquinone in ref 3). The main reason for this conclusion is the absence of the triplet state. This probably arises from reaction of the triplet state with the dihydrophenazine present to yield the semiquinone.



This reaction has been observed in the acridine system<sup>2</sup> and with phenazine in unbuffered alcohol solution.<sup>3</sup> The observed first-order decay coupled with the disappearance of the stable cation radical indicates that the new intermediate, presumably the semiquinone, reacts with the cation radical to yield a new photoproduct. The mass spectrum of the photoproduct solution, with four peaks between 356 and 361 amu, indicates that the photoproduct is a phenazine dimer ( $\text{P}_2 = 360 \text{ amu}$ ,  $\text{P}_2\text{H}_2 = 362 \text{ amu}$ ). Therefore, under the above conditions it would seem that eq 7 is applicable. The nmr



of the photoproduct solution is consistent with that reported for the anthracene photodimer.<sup>19</sup> However, there is no indication of any amine protons, which would be necessary if the dimer is  $\text{P}_2\text{H}_2$ . Unfortunately, there is a possibility that absorption arising from such hydrogen atoms is hidden under the intense aromatic hydrogen absorption so that no definite assignment of the dimer structure is possible.

**Acknowledgment.** This work was carried out under Atomic Energy Commission Contract No. AT-11-1-904. The authors would like to thank Dr. John Wiesenfeld for his help in the design and construction of the flash spectroscopy system and Mr. Anthony Brauner and Miss Karen Brocco for their assistance with some of the experiments.

(19) W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69**, 2022 (1965).