some uncertainty presently exists about the value of the rate constant (k_{-2}) for this reaction and, hence, about the pK_a of $Co(CN)_5H^{3-}$. Kinetic measurements on the oxidation of $Co(CN)_5H^{3-}$ by $Fe(CN)_6{}^{3-}$ (which obeys the rate law $-d[Co(CN)_5{}^{3-}]/dt = 1.2 \times 10^{-1}[Co(CN)_5H^{3-}][OH^-]$ M sec^{-1}, interpreted in terms of eq 6 as the rate-determining step) have yielded a value of 1.2×10^{-1} M^{-1} sec^{-1} for k_{-2} (at 20° and 1 M ionic strength).[4] This, in turn, yields an equilibrium quotient (k_2/k_{-2}) of *ca.* 1×10^6 for reaction 2, corresponding to a pK_a of *ca.* 20 for $Co(CN)_5H^{3-}$. A similar value of k_{-2} (9.7×10^{-2} M^{-1} sec^{-1} at 24°) has recently been determined by Lim and Anson from kinetic measurements on the reaction of $Co(CN)_5H^{3-}$ with $Hg(CN)_2$.[3] It should be noted, however, that these values of k_{-2} are too small to be compatible with the interpretation proposed by Hanzlik and Vlček for the reaction between $Co(CN)_5H^{3-}$ and benzoquinone, in terms of a mechanism also involving reaction 6 as a component step.[2] The origin and significance of this apparent discrepancy are presently unclear and warrant further investigation.

$$Co(CN)_5H^{3-} + OH^- \xrightarrow{k_{-2}} Co(CN)_5{}^{4-} + H_2O \qquad (6)$$

The $Co(CN)_5{}^{4-}$ ion, which we have detected and spectrally characterized for the first time, is isoelectronic with several other known five-coordinate d^8 complexes such as $Fe(CO)_5$, $Mn(CO)_5{}^-$, and $Ni(CN)_5{}^{3-}$.[14,15] With the possible exception of $Ni(CN)_5{}^{3-}$ (which, in the solid state, has been reported to exist in a square-pyramidal, as well as a distorted trigonal-bipyramidal, modification),[15] these species are all believed to have trigonal-bipyramidal configurations and it seems likely that this is the case also for $Co(CN)_5{}^{4-}$. Since the structure of $Co(CN)_5{}^{3-}$ is square pyramidal[16] and that of $Co(CN)_5H^{3-}$ presumably octahedral, it seems likely that both reactions 1 and 2 are accompanied by significant configurational changes. The value of k_{-2}, which seems remarkably low for a highly favorable proton-transfer reaction, may reflect this constraint.

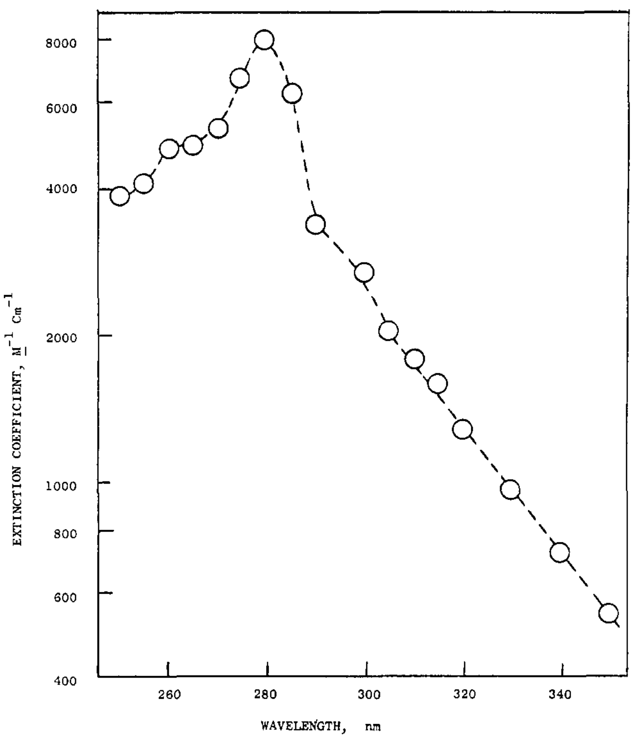

Figure 5. Absorption spectrum of $Co(CN)_5{}^{4-}$ computed from absorbance changes accompanying reaction 1 (corrected for absorbance change due to $Co(CN)_5{}^{3-}$ consumed).

Acknowledgments. This work was performed under the auspices of the U. S. Atomic Energy Commission, with partial support through a fellowship award (to G. D. V.) from the Argonne Universities Association and through grants to the University of Chicago from the National Science Foundation and the National Institutes of Health. We are grateful to Dr. E. J. Hart for valuable guidance and stimulating discussions and to Miss P. D. Walsh, Mr. R. M. Clarke, Dr. B. D. Michael, Mr. B. E. Cleft, and the Argonne linac staff for technical assistance.

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(15) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 1362 (1968).

(16) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3356 (1967).

Photoreduction of Nitrogen Heterocycles. I. The Photoreduction of Phenazine: Evidence for Singlet-State Reactivity

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Abstract: The photoreduction of phenazine by isopropyl alcohol (IPA), triethylamine (TEA), and tri-*n*-butylstannane (TBS) has been studied by kinetic and flash-photolytic methods. All reactions produced 5,10-dihydrophenazine as the major reduction product. The three reactions were determined to proceed, at least mostly, from the nπ^* singlet excited state of phenazine. The reactions with TEA and TBS are much more efficient than the isopropyl alcohol reaction. The rate constants for the TEA and TBS reactions were determined to be $\geq 10^9$ l. mol^{-1} sec^{-1}, while that for the IPA reaction was found to be about 10^3 times slower.

Although kinetic and mechanistic studies of carbonyl photoreductions are legion,[1] relatively little effort has been devoted to such investigations of the photoreduction of nitrogen heterocycles.[2] This is surprising

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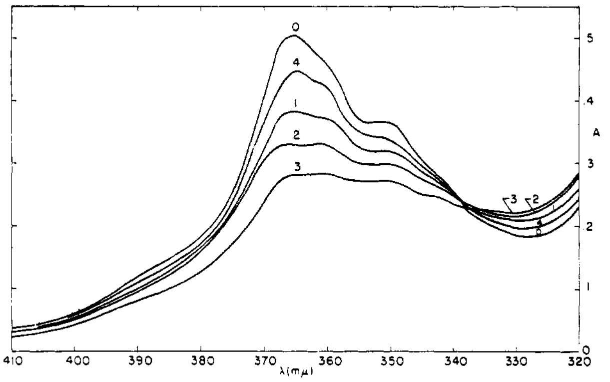

Figure 1. Spectral changes during the reaction of phenazine with 0.095 *M* tri-*n*-butylstannane. Curve 4 shows regeneration of phenazine after 1-hr exposure of the irradiated solution to the atmosphere; curve 0, before irradiation; curve 1, after 3.15 min of irradiation; curve 2, after 642 min; curve 3, after 10.3 min.

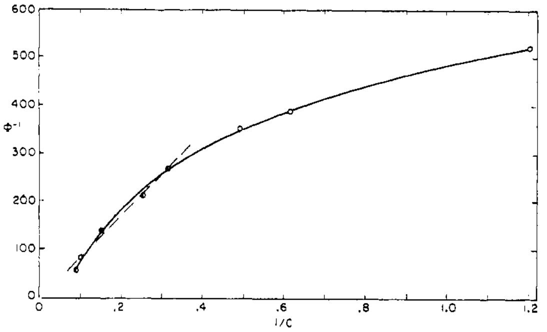

Figure 2. Reciprocal quantum yield *vs.* reciprocal concentration for the photoreduction of phenazine by 2-propanol in benzene. The slope of the dashed line is roughly 850 *M*.

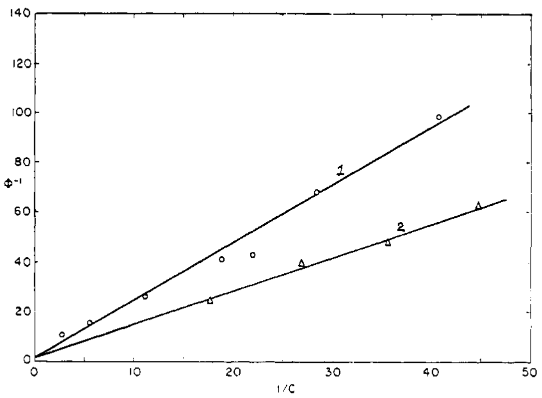

Figure 3. Reciprocal quantum yield *vs.* reciprocal reducing agent concentration for the photoreduction of phenazine by triethylamine, curve 1, slope 2.36 *M;* and by tributylstannane, curve 2, slope 1.40 *M*.

in light of the many examples of heterocyclic photoreduction appearing in the literature[3] and the very great interest which has been shown in the spectroscopic states of these compounds.[4]

We wish here to report on a kinetic study of the photoreduction of phenazine by isopropyl alcohol (IPA), tri-*n*-butylstannane (TBS), and triethylamine (TEA), with the long-range aim of correlating photoreactivity with excited-state properties for a series of nitrogen heterocycles.

The photoreduction of phenazine by air-free IPA has been found by Dufraisse[5] to give 5,10-dihydrophenazine, which immediately reverts back to phenazine upon exposure to the atmosphere. Toromanoff[6] noted the formation of colored crystals during photolysis of concentrated phenazine solutions, and found these to be molecular complexes of phenazine and 5,10-dihydrophenazine of varying stoichiometry. Irradiation of phenazine in acidic alcohol produces the phenazine radical from protonated phenazine *via* an electron-transfer mechanism. The product is either 5,10-dihydrophenazine or the phenazinium radical cation, depending on the acidity of the medium.[7]

Results

Our experimental approach was as follows. Solutions containing 2.1 × 10^{-4} *M* phenazine and various concentrations of the reducing agent were made up in 1-cm optical cells which were deoxygenated and sealed. The absorption spectra of these reactant solutions were then recorded and the cells were irradiated for a series of known time intervals employing the monochromated 366-mμ band of a Hg lamp. After each timed interval, the spectrum was again recorded so as to provide rate data in moles/liter of product conversion per unit time interval of irradiation. These rates were then converted to quantum yields by use of the ferrioxalate actinometer, as described elsewhere.[8]

For each reaction the 365-mμ band of phenazine was seen to decay upon irradiation with clean production of the less intense 348-mμ dihydrophenazine band. An isosbestic point was displayed at 337 mμ, as shown in Figure 1 for reaction with TBS. Exposure of the reaction ampoules to air after irradiation gave >80% regeneration of phenazine within seconds for reactions employing all three reducing agents. The results of the quantum yield *vs.* reducing agent concentration experiments are plotted conventionally as reciprocals in Figures 2 and 3 for the isopropyl alcohol reaction and the TBS and TEA reactions, respectively. An attempt was also made to use toluene as a reducing agent; however, phenazine disappearance in neat toluene was found to have a quantum yield of only ~0.002, and such a slow reaction was deemed unsuitable for further kinetic study.

Rate experiments employing ferric acetylacetonate [$Fe(AA)_3$] as a quencher were also performed. These experiments were done as described above except that low concentrations of the iron salt were introduced into

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(1) For a recent review, see N. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967.

(2) The photoreduction of acridine has, however, been looked at in some detail. See A. Kellman, *J. Chim. Phys.*, **63**, 936 (1966) and references therein.

(3) In addition to the references given throughout this text pertaining to phenazine reduction, see, for example (a) H. Göth, P. Cerutti and H. Schmid, *Helv. Chim. Acta*, **48**, 1395 (1965); (b) P. Cerutti and H. Schmid, *ibid.*, **45**, 1992 (1962); (c) *ibid.*, **47**, 203 (1964); (d) F. R. Stermitz, C. C. Wei, and W. H. Huang, *Chem. Commun.*, 482 (1968).

(4) For recent work containing extensive references, see, for example, (a) B. Krishna, *J. Mol. Spectrosc.*, **13**, 296 (1964); (b) H. Gropper and F. Dörr, *Ber. Bunsenges. Phys. Chem.*, **67**, 46 (1963); (c) F. Dörr and H. Gropper, *ibid.*, **67**, 193 (1963); (d) F. Dörr, H. Gropper, and N. Mika, *ibid.*, **67**, 202 (1963).

(5) C. Dufraisse, A. Etienne, and E. Toromanoff, *C. R. Acad. Sci.*, **235**, 759 (1952).

(6) E. Toromanoff, *Ann. Chim. (Paris)*, **1**, 115 (1956).

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

(8) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 7.

Table I. Attempted Quenching of the Photoreduction of Phenazine in Benzene Solution by $Fe(AA)_3$[a,b]

Expt no.	Reducing agent (M)	[Quencher], M	Φ_0/Φ
1	TBS (0.35)	1.2×10^{-4}	1.14
2	TBS (0.17)	5.6×10^{-5}	0.95
3	TBS (0.086)	5.6×10^{-5}	1.22
4	IPA (6.65)	5.6×10^{-5}	3.21

[a] A slow photochemical reaction occurred during the course of the photolyses which consumed some of the $Fe(AA)_3$. At most 15–20% of the quencher had reacted at the end of the photolyses. [b] At most 8% of the radiation (366 mμ) was absorbed by $Fe(AA)_3$ in these experiments. The results have not been corrected for this.

the reactant solutions. Our results are summarized in Table I.

Flash photolysis was used to determine the rate constant for deactivation of a transient produced upon irradiation of 0.73×10^{-4} M phenazine in benzene solution. (See Experimental Section for details.) Data for the decay of this transient conformed well to a first-order plot which yields a value of ~130 μsec for its lifetime, or a rate constant for deactivation, k_d, of 7.7×10^3 sec^{-1}. This result agrees well with a k_d of ~4×10^3 sec^{-1} found by Buettner[9] for decay of the phenazine transient in benzene solution. This transient, whose $T \rightarrow T'$ absorption spectrum shows a peak at 440 mμ, has been assigned to the $\pi\pi^{*3}$ state of phenazine.[7,9]

Discussion

In isopentane the lowest energy singlet–singlet transition of phenazine has been assigned as an $n \rightarrow \pi^*$ transition.[10,11] In benzene solution this peak appears as a shoulder entered at ~390 mμ on the long-wavelength side of the lowest energy $\pi \rightarrow \pi^*$ band which peaks at about 365 mμ. The latter assignment was made by Lonstauneau.[12] Goodman and Harrel[13] have assigned a $\pi\pi^*$ configuration to the lowest triplet state (15,500 cm^{-1}), which was first observed by Lewis and Kasha.[14] They[13] have also calculated that the $n\pi^{*3}$ state lies between 18,900 and 20,800 cm^{-1}, although no experimental evidence for this energy has been reported.

In considering the mechanistic photochemistry of phenazine, we must therefore *a priori* take cognizance of at least three potentially reactive states. The $\pi\pi^{*1}$ state may be immediately disqualified as the reactive state in at least the TBS and TEA reactions by the following argument. The slopes of curves 1 and 2 of Figure 3 may be theoretically identified with the ratio k_d/k_r, where the symbols refer to rate constants for deactivation and reaction (*i.e.*, H-atom abstraction) for the reactive excited state.[15] The slopes of the lines in Figure 3 are 2.36 and 1.40 M for the TEA and TBS reactions, respectively. Therefore, k_d and k_r are, for these reactions, of comparable magnitude. By consideration of the absorption spectrum of phenazine and by the observation that the molecule displays no fluorescence, it may be calculated[16] that k_d for the $\pi\pi^{*1}$ state must be greater than 10^{11} sec^{-1}. Thus, if the $\pi\pi^{*1}$ state were the reactive state, the slopes of Figure 3 would necessitate that k_r be greater than 10^{11} l. mol^{-1} sec^{-1}. This number, however, is greater than the rate constant for diffusion-controlled collision of small molecules in benzene at room temperature.[17] Therefore, the $\pi\pi^{*1}$ state cannot be a significant reactive state in the TBS or TEA photoreductions.

Let us now assume the $\pi\pi^{*3}$ state to be the photochemically reactive state. It is this state which gives rise to the first-order transient produced upon flash photolysis of phenazine in benzene.[7,9] Since we have ascertained a lifetime of 130 μsec for this transient, k_d for the $\pi\pi^{*3}$ state equals 7.7×10^3 sec^{-1}.[18] But if this is the reactive state, then $k_r = 5.5 \times 10^3$ l. mol^{-1} sec^{-1} from Figure 3, curve 2. By employing the data of Table I for quenching of this reaction, we will now show that it is unlikely that the $\pi\pi^{*3}$ is the major reactive state in photoreduction by TBS.

For a triplet reaction carried out in the presence of a triplet quencher, a kinetic derivation[1] leads to the expression

$$\Phi_0/\Phi = 1 + (k_q[Q]/[k_d + k_r[C])$$

where Φ_0 is the quantum yield in the absence of quencher and Φ is the same in the presence of a triplet quencher of concentration [Q], k_q is the rate constant for quenching, [C] is the reactant (*i.e.*, reducing agent) concentration, and k_d and k_r are as defined above. Now, assuming triplet quenching to be essentially diffusion controlled, $k_q = 3 \times 10^9$ l. mol^{-1} sec^{-1}.[19] Substituting this value along with the concentrations of quencher and TBS given in experiment no. 3 of Table I, as well as values of 7.7×10^3 sec^{-1} and 5.5×10^3 M^{-1} sec^{-1} for k_d and k_r into the expression above, allows calculation of $\Phi_0/\Phi = 21.4$. The experimental value of $\Phi_0/\Phi = 1.22$ is well over an order of magnitude less than this theoretical result.[20] For this reason, we feel it unlikely that the $\pi\pi^{*3}$ is the important reactive state in these photoreductions. We are thus forced to consider the $n\pi^{*1}$ state as at least the *major* reactive state

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

(10) L. Goodman and R. Harrel, *J. Chem. Phys.*, **30**, 1131 (1959).

(11) The existence of two low-lying $n\pi^*$ singlet states has been suggested by Höchstrasser; see R. M. Höchstrasser, *ibid.*, **36**, 1808 (1962).

(12) P. Lonstauneau, G. Nonchi, and A. Rousset, *C. R. Acad. Sci.*, **257**, 2928 (1963).

(13) L. Goodman and R. Harrel, *J. Chem. Phys.*, **30**, 1131 (1959).

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

(15) For a treatment of photochemical kinetics on which this assertion is based, see ref 1, Chapter 6. Note that the identification of the slope with k_d/k_r is strictly valid only if *one* excited state is reactive. The apparent linearity of the plots shown in Figure 3 tends to support, but does not prove this supposition.

(16) See ref 1, Chapter 4, for a simple discussion of this calculation.

(17) Various calculations assign a value of roughly 5×10^9 M^{-1} sec^{-1} to k_{diff} under the conditions of our experiments; see, for example, G. M. Harris, "Chemical Kinetics," D. C. Heath, Boston, Mass., 1967, p 87.

(18) We do not intend to imply that this result gives the *true* nonradiative triplet lifetime of phenazine in benzene solution, but rather only the lifetime under the condition of our photochemical experiments. We are well aware of the pronounced affect that adventitious impurities can have on flash-photolytic determinations of solution lifetimes. Our confidence in at least the rough accuracy of this number is somewhat increased, however, by the findings of other groups, which assign k_d in benzene to be ~4×10^3 and ~2×10^3 sec^{-1} in water (ref 9), about 25×10^3 sec^{-1} in several alcohols, and about 14×10^3 sec^{-1} in freon (ref 7).

(19) It has been found that $Fe(AA)_3$ quenches the photoreductions of 1-naphthaldehyde with a rate constant of ~3×10^9 M^{-1} sec^{-1}; see J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963). Furthermore, $Fe(AA)_3$ is a more effective quencher than ferric dipivaloyl methide, by a factor of 5.4: G. S. Hammond and R. P. Foss, *J. Phys. Chem.*, **68**, 3739 (1964). The latter is known to quench the benzophenone triplet with a rate constant of at least 1×10^9 M^{-1} sec^{-1}.

(20) Using the results of other experiments in Table I shows an even greater discrepancy between experimental and theoretical values of Φ_0/Φ.

in the TBS and TEA photoreductions. The rate constant for deactivation of this state, k_d, has been calculated to be $\geq 10^9$ sec^{-1} by absorption spectrum and emission considerations.[7] With reference to Figure 3, we therefore see that $k_r \geq 10^9$ l. mol^{-1} sec^{-1} for these reactions. The $n\pi^{*1}$ state apparently reacts with TBS and TEA with rate constants which are within an order of magnitude of that predicted for diffusion-controlled reactions.

It is noteworthy that Hercules,[7] in a study of the photoreduction of phenazine by acidic methanol, invoked the protonated $n\pi^{*1}$ of phenazine as the reactive state in an electron-abstraction reaction[21] yielding either dihydrophenazine or the phenazinium radical cation. The $n\pi^{*1}$ state of acridine may also be reactive in the photoreduction of that compound.[22]

The results for the isopropyl alcohol reduction shown in Figure 2 are worthy of some discussion. The falloff in quantum yield with decreasing IPA concentration is very dramatic, and shows marked curvature. (However, the latter point will not be belabored, owing to the very low quantum yields evident from the plot, and the effective change in solvent environment over the concentration range studied.) The slope of *ca.* 850 *M* apparent at the high-concentration end of Figure 2 would demand a value of k_r of 10^0–10^1 M^{-1} sec^{-1} if the $\pi\pi^*$ triplet state were reactive. By the argument offered above for the TEA and TBS reactions, we would expect a value of $\Phi_0/\Phi \simeq 10^4$ for triplet quenching using the data of Table I, experiment no. 4. The observed value of $\Phi_0/\Phi = 3.21$ is thus clearly inconsistent with a reactive $\pi\pi^*$ triplet. We therefore propose the $n\pi^*$ singlet to be the reactive state in this reaction. By the slope of Figure 2, the rate constant for reaction from this state must be about 10^6 l. mol^{-1} sec^{-1} or greater.

The apparent lack of reactivity of the long-lived $\pi\pi^{*3}$ state of phenazine, even with reagents as reactive as TBS, is worthy of note.[23] We suspect that perhaps the low triplet energy of phenazine (42 kcal/mol) may be responsible for its low reactivity, either because of simple energetics, or because little $n\pi^*$ "character" is imparted to the lowest $\pi\pi^*$ triplet by what may be a large energy separation between these two states.[24] We are presently engaged in investigating the kinetics of other diaza heterocycles including several benzo-condensed homologs of phenazine and quinoxaline, which have higher triplet energies than phenazine itself, in an effort to clarify this point.

Experimental Section

Materials. Phenazine (Aldrich Chemical Co.) was purified by twice recrystallizing from ethanol, mp 172–173° (lit.[25] mp 171°). Benzene (Mallinckrodt analytical reagent) was purified by distillation over P_2O_5 through a 5-ft glass bead column, and a center fraction was collected. Toluene (Fisher certified) was purified the same way. Isopropyl alcohol (Burdick and Jackson "distilled in glass" reagent) was used without further purification. Triethylamine was purified by slow fractional distillation through a 4-in. vacuum-jacketed glass helices column. Tri-*n*-butylstannane was prepared by $LiAlH_4$ reduction of tri-*n*-butyl chloride following the method of Luitjen,[26] and subsequently purified by fractional vacuum distillation. Ferric acetylacetonate (MacKenzie Chemical Works, Inc.) was used without further purification.

Photochemical Kinetics. Kinetic data were obtained in the following way. The solution to be irradiated (4 ml) was entered into a 1-cm rectangular Beckman Pyrex spectrometer cell fitted with a constricted cylindrical stem. These cells were deoxygenated under vacuum by several freeze–thaw cycles and flame sealed. The absorbance of the phenazine peak at 365 mμ was recorded using a Beckman DK spectrometer. A voltage-stabilized GE BH-6 Hg lamp was focused into a Bausch and Lomb monochromator to isolate the 366-mμ band, and the transmitted band was focused onto the reactant solution. After irradiation for timed intervals, the phenazine absorbance was noted. For each concentration of reducing agent (or of quencher), a minimum of five points was used to construct a per cent reaction *vs.* time plot. Good linearity was generally obtained for up to 25% reaction. Initial rates as a function of time were obtained by multiplying the slopes by the initial phenazine concentrations. These rates were then converted to quantum yields by use of the ferrioxalate actinometer,[8] or in the case of the quenching experiments, simply reported as relative rates.

Flash Photolysis. The flash apparatus has been described elsewhere.[27] A solution of phenazine (0.73×10^{-4} *M*) was made up using the same benzene sample as that used in the continuous-irradiation experiments described above. The solution was entered into a 6-cm path length Pyrex optical cell end, and degassed by several freeze–thaw cycles on a vacuum line. The cell was then wrapped in a blue plastic Roscolene filter, No. 963, which passes light between 350 and 530 mμ (T_{max} = 410 mμ). The sample was flashed at an input energy of 900 J. Decay curves were measured after this time by oscilloscope displays at selected wavelengths. Changes in optical density as a function of time were found with the aid of a Gerber GDDRS-3B-2 data reduction system, yielding a good fit to a first-order kinetic plot.

Acknowledgments. We wish to thank Drs. J. Robert Huber and Robert Wiener for helpful discussion of our results.

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(21) We feel it unlikely that this mechanism obtains in our photoreductions in neutral solution.

(22) See E. Van der Donckt and G. Porter, *J. Chem. Phys.*, **46**, 1173 (1967). Other reactive states have been invoked by other workers, but on less convincing evidence; see ref 2 and 9.

(23) By contrast, the $\pi\pi^{*3}$ states of the carbonyl compounds 2-acetonaphthone and 1-naphthaldehyde react with TBS in benzene with rate constants of 9.0×10^5 and 5.5×10^6 M^{-1} sec^{-1}, respectively; see ref 19.

(24) See ref 13 in this connection.

(25) "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

(26) G. J. M. Van der Kerk and J. G. A. Luitjen, *J. Appl. Chem.*, **7**, 369 (1957).

(27) P. A. Schnieper, *NEREM Rec.*, 158 (1965).