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STUDIES OF NITROGEN HETEROCYCLE PHOTOREDUCTION, II: THE PHOTOREDUCTION KINETICS OF DIBENZO/a,c/PHENAZINE

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In a recent kinetic study of the photoreduction of phenazine by isopropanol, triethylamine or tri-n-butylstannane, we concluded that reactivity occurs from the low-lying $n\pi^*$ singlet state.[2] It was suggested that the unreactivity of the long-lived $\pi\pi^*$ triplet of phenazine might be related to its very low energy of about 44 kcal/mole.[3,4] We are currently investigating the photoreduction of several structural homologs of phenazine in an effort to clarify the factors influencing photoreactivity in the nitrogen heterocycles. In this report we describe our kinetic results for the photoreduction of dibenzo/a,c/phenazine (DBP) by tri-n-butyl stannane (TBS). DBP has a lowest $\pi\pi^*$ triplet, 53 kcal/mole above the ground singlet and a low-lying singlet state also of $\pi\pi^*$ configuration.[5]

DBP (Aldrich) was purified by crystallization from benzene, mp 223-5°, lit.[6], 223°. TBS was prepared as described by Luitjen.[7] Air-free solutions of DBP and TBS were prepared and irradiated as previously described;[2] the extent of reaction was monitored by recording spectral changes after timed periods of irradiation. The DBP maxima at 395 and 375 nm decrease upon irradiation and a broad band, 500-320 nm, is produced (Figure 1). As in the case of phenazine photoreduction, exposure of the irradiated solutions to air resulted in instantaneous re-oxidation of the reduction product back to the starting compound. Irradiation of DBP in the presence of triethylamine (a potent photochemical reducing agent) produces the same spectral changes seen in Figure 1. Phenazine is also photoreduced by triethylamine yielding 5,10-dihydrophenazine.[8,9] No reaction occurs upon irradiation of DBP in the absence of TBS. Thus we feel certain that the product is reduced at the nitrogen atoms giving secondary diamine analogous to 5,10-dihydrophenazine.

Monochromatic light (395 nm) was used for quantum yield determinations relative to the ferrioxalate actinometer.[10] Quantum yields at 5 TBS concentrations varied from 1.0 at .1M TBS

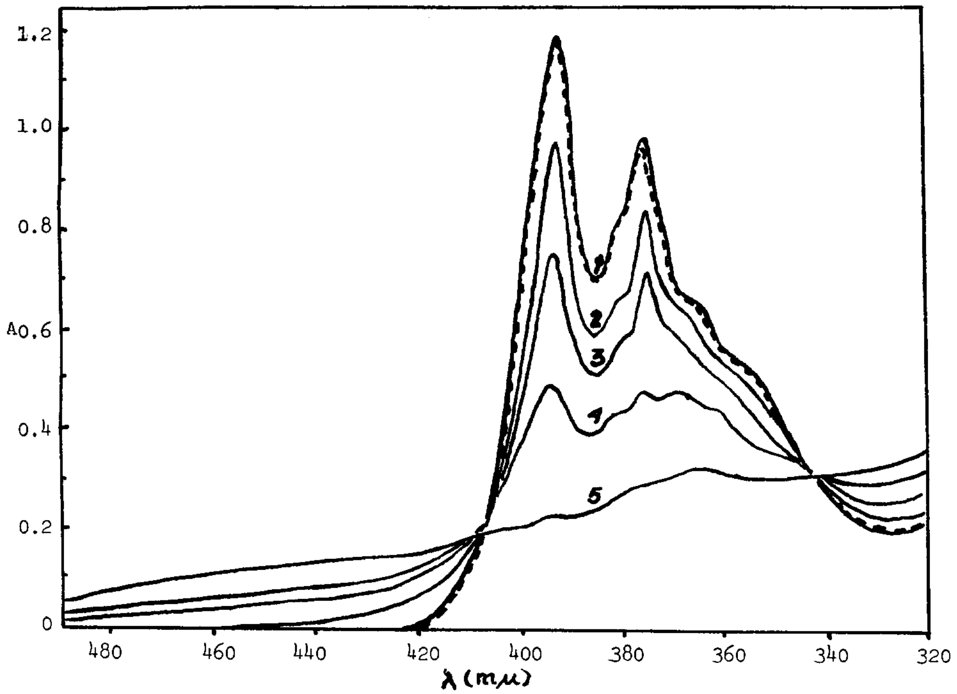

Figure 1. Spectral changes occurring upon irradiation of dibenzo/a,c/phenazine in benzene solution with 0.05 M tributylstannane. Before irradiation, 1; After 1 minute irradiation, 2; After 3 minutes irradiation, 3; After 7 minutes irradiation, 4; After 12 minutes irradiation, 5; After exposure of the irradiated solution to air, dashed line.

to 0.27 at .01M TBS. These values are somewhat approximate due to relatively large corrections (ca. 20%) applied for decreasing absorption by the DBP and competitive absorption by the reaction product. A linear plot of Φ^{-1} vs $(TBS)^{-1}$ was found with a slope of 0.03M. Ferric acetylacetonate was then used as a quencher for the reaction of DBP with 0.024M TBS, and results plotted as Φ_0 / Φ vs $Fe(AA)_3$, displaying a slope of $3x10^{4}M^{-1}$.

Attempt was made to quench the fluorescence of DBP with TBS so as to assess the amount of singlet reaction which may be occurring. A $5x10^{-4}M$ solution of DBP in deoxygenated benzene was subjected to irradiation in a Farrand spectrophosphorimeter. No quenching of the DBP fluorescence (λ_{max}425nm) was observed when TBS was introduced even at concentrations as high as 0.1M where DBP was found to react with quantum yields of ca. 0.9- 1.0. Thus, the fluorescent $\pi\pi^*$ singlet state[5] of DBP is not measurably reactive in this system.

The rate constants for triplet reaction and decay may be estimated from the slopes of the Φ^{-1} vs $(TBS)^{-1}$ and Stern-Volmer quenching plots.[11] From the former, $k_d/k_r=0.03M$, and from the latter, $k_q/[k_d+k_r(TBS)] = 3\times10^{4}M^{-1}$. Since k_q for triplet quenching[12,13] by $Fe(AA)_3$ is in the range of $3\times10^{9}M^{-1}sec.^{-1}$, we may estimate that $k_d \sim 5.7\times10^{4}sec^{-1}$ and $k_r \sim 1.9\times10^{6}M^{-1}sec^{-1}$. (Flash photolysis of DBP in benzene produces a transient which decays with a first-order rate constant of $1.4\times10^{4}sec^{-1}$, in fair agreement with the k_d found in the quenching experiment.[14])

The observed electronic energy levels of phenazine and dibenzophenazine and reactivity of each is summarized in Figure 2.

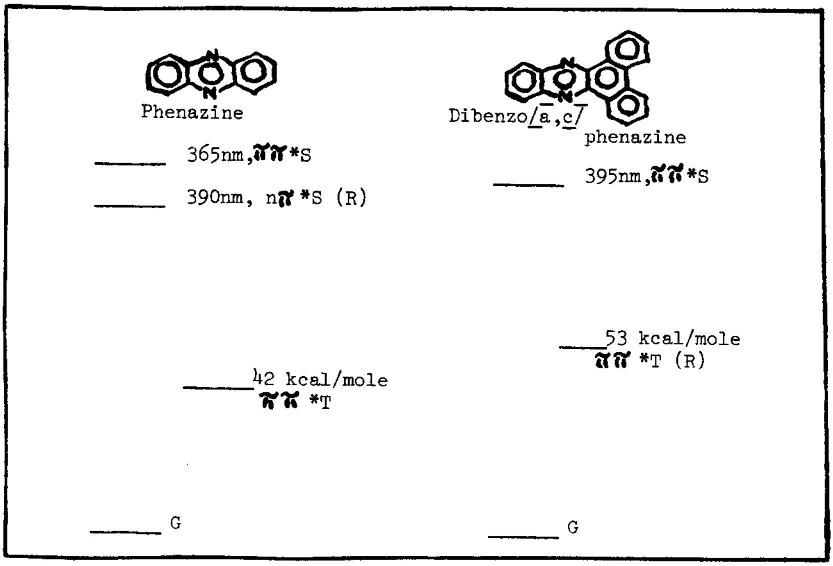

Figure 2. Observed excited states of phenazine and dibenzo/a,c/phenazine. Reactive states are indicated by (R). See Refs. 3, 4, and 16.

We conclude that DBP is photoreduced by TBS from the ππ * triplet state of the former in contrast to phenazine which photoreduces from its nπ * singlet.[2,15] It may be that in general only nitrogen heterocycle singlets with a lowest nπ * configuration show high reactivity toward photoreduction, while ππ * triplets may be reactive provided they possess a certain minimal energy or degree of mixing with an upper nπ * state. In this connection we are presently studying the photoreduction of quinoxaline which has both an $n\pi^*$ lowest singlet and high energy $\pi\pi^*$ triplet.

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