

THE REACTIVE EXCITED STATES OF ACRIDINE AND PHENAZINE IN SOLUTION: A FLASH PHOTOLYSIS ELECTRON SPIN RESONANCE AND CHEMICALLY INDUCED DYNAMIC ELECTRON POLARIZATION STUDY

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Summary

The free radicals formed on reaction of the excited states of acridine and phenazine with suitable hydrogen donors are produced in an electron-spin-polarized state. From the phases of their electron spin resonance signals it is concluded that, whilst acridine reacts through an excited singlet state, phenazine reacts through an excited triplet one. The precise nature of these states is discussed.

1. Introduction

The UV photoreduction of many aza-aromatic compounds in alcohol solutions, in the absence or presence of an amine, proceeds via free-radical intermediates. These often may be detected and identified within a few microseconds of their formation using flash photolysis electron spin resonance (ESR) methods. They are almost invariably observed to be electron spin polarized, *i.e.* the relative populations of the electron energy levels differ from those at thermal equilibrium. The process is known as chemically induced dynamic electron polarization (CIDEP) (see for example ref. 1). The type and phase of the CIDEP observed in the initially formed radicals exposes the multiplicity and nature of the excited state of the molecule which was their precursor. The phenomenon has been used previously to investigate the reactive states in diazanaphthalene [2, 3] and methyl pyrazine [4] molecules, and is extended here to acridine and phenazine.

Two different processes, which yield polarized spectra with different characteristics, yield electron polarization immediately after the radicals are created in a photolysis flash. In the triplet mechanism (TM) spin polarization is created in the triplet state of a molecule if, as usually happens, the intersystem crossing (ISC) from the initial excited singlet occurs at different rates into the three zero-field split sublevels of the triplet. This process is

controlled by selection rules which are constrained by the molecular symmetry; spin-orbit coupling connects states of the same overall symmetry. The system then evolves in the magnetic field of the spectrometer to yield a polarization in the Zeeman levels of the laboratory frame. Rapid reaction of the polarized triplet, with conservation of spin alignment, yields a pair of radicals, each polarized in the same sense. Whether this is absorptive or emissive depends both on which state is populated preferentially in the triplet precursor and on whether it lies above or below the barycentre of the triplet sublevels, *i.e.* on the sign of the zero-field splitting parameter.

The radical pair mechanism (RPM), in the form important here, operates in the geminate pair of radicals produced when an excited singlet or triplet state is quenched. It is a spin-sorting process which causes the spectra of radicals born from triplets to change phase from emission to absorption (an E-A pattern) as the spectrometer field is increased. In contrast, spectra of radicals created from singlets exhibit A-E patterns. With dissimilar radicals one spectrum is more emissive than the other, the precise CIDEP spectrum observed depending on the specific radicals concerned.

Both the TM and the geminate RPM processes occur before observations start and the spectra often show the effects of each. A TM effect immediately indicates a triplet state to be involved, and then the RPM usually produces an additional E-A distortion. An A-E pattern is an unequivocal illustration of the reaction of a singlet. The natures of the reactive excited states of acridine and phenazine have been the subject of many studies and some controversy. There is good evidence that the photoreduction of acridine in amines and alcohols results from the quenching of an excited singlet state [5, 6]; the position with phenazine is less clear and both excited singlet [7] and upper triplet states [8] have been proposed. Both compounds are excellent candidates for a transient ESR study.

2. Experimental details

Flash photolysis ESR spectra were obtained using the time integration spectroscopy technique described recently in experimental and theoretical form [9, 10]. Photolysis was performed at 308 nm, using a Lambda-Physik EMG 101 laser operating on the XeCl transition with a pulse energy limited to about 20 mJ pulse⁻¹; all the incident light was absorbed in all solutions. The ESR spectra were obtained using unmodulated detection in a modified Bruker ER 200D spectrometer.

Samples, obtained from the Aldrich Company and recrystallized from ethanol, were irradiated as about 10⁻² M solutions in pure propan-2-ol and octan-2-ol, in mixed alcohol-triethylamine (10:1) and in mixed hexane-triethylamine (10:1). Since the experiment involves many thousands of flashes to obtain the complete ESR spectrum the sample flowed through the irradiation region to avoid substrate depletion and photolysis of reaction products. All experiments were conducted at 15 °C.

3. Results

In Fig. 1 is shown the spectrum observed, with time integration between 0.98 and 2.20 μs after the photolysis flash, of the radical formed from phenazine by hydrogen abstraction from triethylamine. As with the radical from acridine (see below) the ESR spectrum of this species has not been reported previously in solution. The spectrum of the counter-radical derived from triethylamine is not observed because of its rapid reaction. Closely similar spectra of the same radical were obtained from phenazine in all the solvents listed above; the spectra display emissive TM polarization with an RPM contribution of the E-A type (appearing as a comparatively small distortion of the line intensities) superimposed. Both contributions demonstrate that a triplet state of phenazine is responsible for reaction.

The identity of the phenazine-derived radical is that shown in the figure, although the complexity of the spectrum with its overlapping lines does not allow all its coupling constants to be measured. The spectrum is sufficiently similar to that obtained from the same radical in the solid state [11] to be confident of its nature.

In Fig. 2 is shown the spectrum of the radical derived from acridine in octan-2-ol-triethylamine solution with time integration between 0.62 and 1.02 μs after the photolysis flash. A similar result was obtained from propan-2-ol-triethylamine solution but no radicals were detected in pure alcohol or hexane-triethylamine solutions. The spectrum shown is unusually weak in the aza-aromatic series, suggesting a comparatively low yield of radicals. It displays an A-E pattern of RPM polarization which shows incontrovertibly that the radicals originated from an excited singlet state. The slight bias in the spectrum towards emission is not due to TM polarization but originates in a dissimilar initial pair of radicals, and serves to identify the counter-radical as the $\text{Me}\dot{\text{C}}\text{HNET}_2$ species. The spectrum is in reasonable agreement

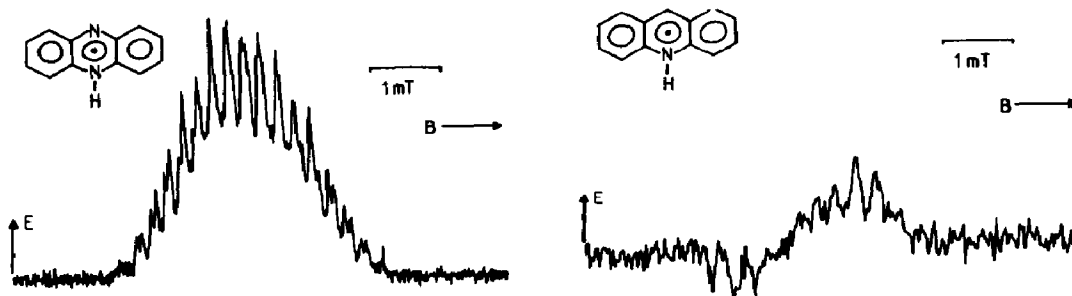


Fig. 1. The spectrum observed on the photolysis of a 0.01 M solution of phenazine in an octan-2-ol-triethylamine mixture. The radical observed from the amine reacts too quickly to be observed in this system. The spectrum shows TM polarization with some E-A RPM distortion.

Fig. 2. The spectrum observed in the photolysis of a 0.01 M solution of acridine in an octan-2-ol-triethylamine mixture; the amine radical is not observed once more. The spectrum shows A-E RPM polarization.

with one calculated using coupling constants obtained in the solid state [11], for the neutral species derived from acridine, which is shown in Fig. 2.

4. Discussion

The excited states of acridine and phenazine in hydroxylic solvents are shown in Fig. 3. The ordering of the $^1\pi\pi$ and $^1n\pi$ states of acridine is solvent dependent and is reversed ($^1n\pi$ lowest) in non-polar solvents such as hexane [12]. In both acridine and phenazine ISC driven by spin-orbit coupling is allowed from the $^1n\pi$ state to the T_1 state, which has $\pi\pi$ character. In the solid state reaction has been demonstrated from the lowest triplet state of acridine, using matrices of hydrogen atom donor molecules [13]; our work has shown, however, that in solution radicals formed by hydrogen atom abstraction originate from an excited singlet state, which may be $^1\pi\pi$ or $^1n\pi$. In alcohol solvents the $^1n\pi$ state has been shown to be populated by thermal activation from the $^1\pi\pi$ [14] and it is likely that the $^1n\pi$ state is the reactive one in our experiments. The lowest triplet state of acridine is undoubtedly populated during photolysis but appears to be unreactive towards hydrogen atom donors in solution; the explanation for this probably lies in its $\pi\pi$ character and its comparatively low energy. The majority of acridine molecules which reach T_1 probably return to the ground state without reaction.

The absence of transient radicals from solutions of acridine in non-polar solvents is puzzling, particularly because the more reactive $^1n\pi$ is expected to be lower than the $^1\pi\pi$ one in such solvents. It has been shown [5] that photoreduction may also occur via a non-radical pathway, and this may predominate in hexane and similar solvents.

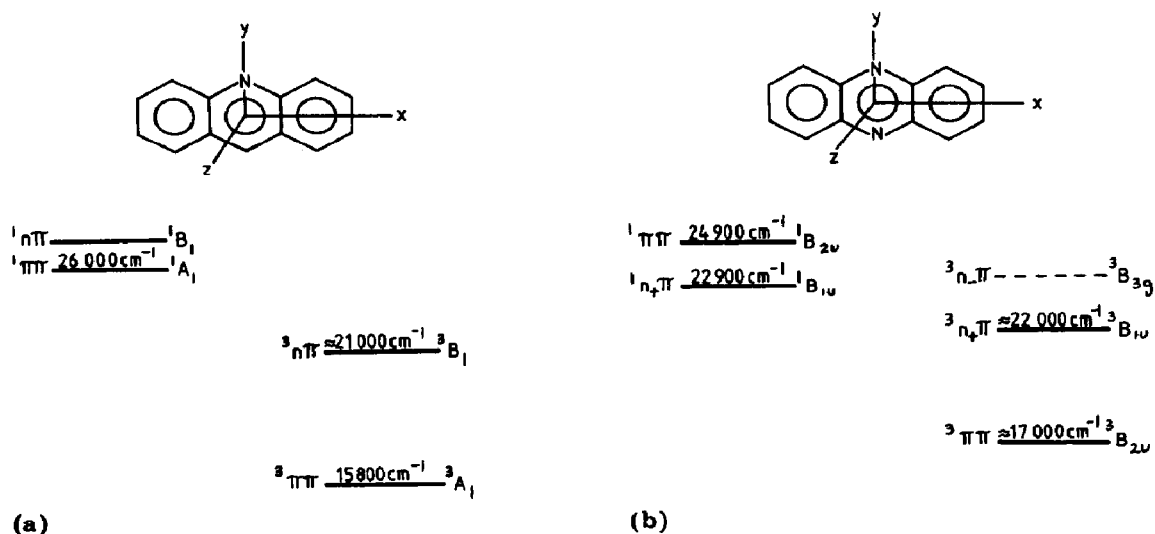


Fig. 3. The excited states of (a) acridine and (b) phenazine in alcohol solution (not to scale).

ESR spectra from solutions of phenazine show clearly that the radical intermediate is formed by the reaction of a triplet state. There is evidence [6, 7] that the lowest triplet state of phenazine is unreactive in solution, being similar in this respect to T_1 in acridine. If this is the case our work implies that an upper triplet state is responsible for photoreduction in phenazine via a radical mechanism, possible candidates being $T_2(n+\pi)$ and $T_3(n-\pi)$. The position of T_3 is uncertain, but on symmetry grounds it is unlikely to be populated from S_1 or S_2 and probably does not figure in photoreduction. Our spectra only give a rough indication of the yield of radicals following the flash photolysis of phenazine but work by other groups indicates that hydrogen atom abstraction from an excited state is the dominant mechanism. The quantum yield of the reduced dihydro form with triethylamine as quencher is about 0.1; the quantum yield of photoreduction is directly related to the ease of hydrogen atom abstraction from the quencher molecule [7]. No other pathways to the reduced form have been detected in phenazine photoreduction, in contrast with the photoreduction of acridine (which has a similar overall quantum yield [5, 6]) in which a non-radical mechanism is also implicated [5].

Some insight into the ISC process can be obtained from the fact that the TM polarization is emissive, *i.e.* ISC is predominantly to a level which lies above the barycentre of the triplet sublevels. Spin-orbit coupling would allow both $S_1(n+\pi) \rightarrow T_1(\pi\pi)$ and $S_2(\pi\pi) \rightarrow T_2(n+\pi)$ transitions; in both cases the T_x sublevel is preferred on symmetry grounds. This then must be an upper level, which implies a positive value for the zero-field splitting parameter. This is consistent with the known nature of the T_1 state but unfortunately the corresponding sign is not known for the T_2 one; although CIDEP in principle might test the hypothesis that T_2 is the reactive state, the information necessary is not yet at hand.

If, as seems likely, T_2 is involved the observation of its reaction has interesting implications as to its lifetime. Even if reaction is near to the diffusion-controlled limit, an unusually slow rate of internal conversion between T_2 and T_1 is implied. The contrast with acridine in the behaviour of phenazine is striking, for no triplet state reaction has been observed from acridine in alcohols or non-polar solvents. This is surprising in view of the similarities between the excited states of these two compounds.

5. Conclusions

Using flash photolysis ESR it has been shown that in mixed alcohol and amine solvents reaction occurs from an excited singlet state in acridine, but from a triplet state in phenazine. The identification of these states is discussed; comparison with previous work suggests that an upper triplet state of phenazine is involved, probably $T_2(n+\pi)$.

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