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QUENCHING OF TRIPLET STATES OF DIAZINES BY H-ATOM DONORS. FORMATION OF AZYL RADICALS

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The laser flash photolysis of pyrazine in water and in organic solvents has been examined. The $^3(n, \pi^*)$ state in water has absorption bands at 230, ≈ 260 , ≈ 295 , ≈ 640 , 700 and 810 nm, and decays with $k = 2.2 \times 10^5 \text{ sec}^{-1}$. It is quenched by oxygen with $k_q = 3.2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ and by various H-atom donors, e.g., $k_q = 1.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ for isopropyl alcohol. On reaction with H-atom donors, the chemistry of $^3(n, \pi^*)$ pyrazine produces the neutral pyrazyl radical and the dihydro radical cation, whose characteristic absorption spectra have been identified. These results are discussed by comparison with $^3(\pi, \pi^*)$ diazines and with $^3(n, \pi^*)$ aromatic carbonyl compounds.

1. Introduction

The electronic spectra and the radiative and radiationless paths for deactivation of excited states of N-heterocyclic compounds have been examined and studied in detail (see refs. [1, 2] for general review). The diazabenzenes are reported [3] to have allowed $^1(n, \pi^*)$ states as the lowest singlet excited states and $^3(n, \pi^*)$ as the lowest triplet states. The diazaphthalenes and diazaanthracenes [1, 2, 4, 5] have $^3(\pi, \pi^*)$ as the lowest triplet states, and their lowest singlet excited states are $^1(n, \pi^*)$. Very little work has been carried out on the chemistry of these (n, π^*) and (π, π^*) excited states, particularly in the case of the diazabenzenes. This is in contrast to the understanding which exists on the chemical reactions of $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ states of aromatic carbonyl compounds.

2. Laser photolysis

Reported below are the results obtained from a laser flash photolysis study of pyrazine and related com-

pounds in solution at 25°C. Optical excitation at 265 nm was carried out using a frequency quadrupled neodymium laser (Holobeam) and single pulses of ≈ 15 nsec duration. Kinetic absorption spectrophotometry of the transient species produced was carried out at right angles to the laser beam, using the light output from a pulsed 250 W Osram xenon lamp (in this way the light output below ≈ 280 nm is increased by a factor of ≈ 400). A temperature-controlled jacketed optical cell was used, with an ≈ 8 mm effective optical path. Complete details will appear elsewhere [6]. Pyrazine (Aldrich, Gold label) was used as received. All reagents used were the highest purity commercially available. Organic solvents were Spectral grade.

Pyrazine has absorption bands in water (pH 6.0) at 261, 268 and 303 nm with extinction coefficients of 5.9×10^3 , 4.3×10^3 and $8.5 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The ground state pK_a of pyrazine is 0.65. On laser photolysis of an oxygen-free (argon saturated) aqueous solution of $1.3 \times 10^{-4} \text{ M}$ pyrazine at pH 5.4, a short-lived transient optical absorption is observed, see fig. 1, which is assigned to the triplet-triplet absorption spectrum of neutral pyrazine. The spectrum has been corrected for depletion of ground-state pyrazine (Pz), assuming that on quenching by an H-atom donor, every ^3Pz gives the neutral pyrazyl radical, whose extinction coefficient is known [7] (see below

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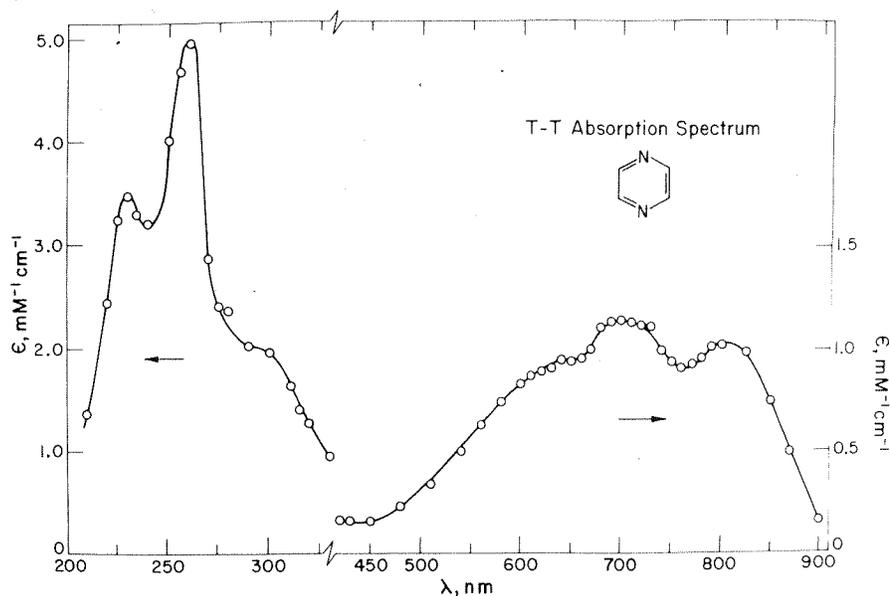


Fig. 1. Triplet-triplet absorption spectrum of pyrazine (1.3×10^{-4} M) in argon-saturated aqueous solution at pH 5.4, obtained by optical excitation at 265 nm using a frequency quadrupled neodymium pulsed laser. Spectrum corrected for depletion of pyrazine ground state (see text). At $\lambda > 450$ nm spectrum obtained in N_2O -saturated solutions in order to remove the absorption spectrum of e_{aq}^- produced from the photoionization of pyrazine.

Table 1

Absorption maxima and extinction coefficients of the triplet-triplet absorption bands of pyrazine in water^{a)}

Absorption maxima (nm) b)	ϵ ($M^{-1} \text{cm}^{-1}$) ^{c)}
230	3.5×10^3
≈ 260	4.9×10^3
≈ 295	2.0×10^3
≈ 640	9.4×10^2
700	1.1×10^3
810	1.0×10^3

a) Argon-saturated solutions at pH 5.4, [pyrazine] = 1.3×10^{-4} M.

b) Spectrum corrected for depletion of ground-state pyrazine.

c) See text for determination of extinction coefficient values to $\pm 20\%$ in λ region 350–900 nm, and $\pm 30\%$ in λ region below 350 nm.

and ref. [8]). The absorption maxima and ϵ are given in table 1. At all wavelengths from ≈ 230 –900 nm, the decay of this transient (or the regeneration of the pyrazine ground state) follows perfect first-order kinetics

with $k = 2.9 \times 10^5 \text{ sec}^{-1}$ in 1.3×10^{-4} M pyrazine solutions. The triplet is produced within the duration of the laser pulse (15 nsec) indicating that the lifetime of the $^1(n, \pi^*)$ excited state is much shorter.

In addition, photoionization of pyrazine is observed with the formation of the characteristic absorption spectrum of e_{aq}^- at ≈ 720 nm. The e_{aq}^- is also formed within the laser pulse and may be produced by a biphotonic process from the triplet state or from the singlet excited state. It is not possible, at this time, to confirm either mechanism.

3. Quenching of $^3(n, \pi^*)$ pyrazine

The observed spectrum of triplet pyrazine (fig. 1) is quenched by oxygen, with a $k_q = 3.2 \times 10^9 \text{ M}^{-1} \text{sec}^{-1}$, supporting the above assignment (see table 2). Self-quenching by ground-state pyrazine has also been found, with a $k_q = 5.8 \times 10^8 \text{ M}^{-1} \text{sec}^{-1}$. Based on this observation, the decay of the $^3(n, \pi^*)$ at "infinite" dilution was found to have $k = 2.2 \times 10^5 \text{ sec}^{-1}$ at pH 7.1.

Addition of good H-atom donors, such as aliphatic

Table 2
Rate constants for quenching of the pyrazine triplet state in water^{a)}

Quencher	pH	λ monitored (nm)	k_q (M ⁻¹ sec ⁻¹) ^{b)}
oxygen	7.1	280	3.2×10^9
pyrazine	7.1	280	5.8×10^8
isopropyl alcohol	6.4	620	1.3×10^8
methyl alcohol	6.4	620	2.7×10^7
<i>tert</i> -butyl alcohol	6.4	620	6.7×10^6
cyclohexane	-	620	1.0×10^7 ^{c)}
acetonitrile	-	280	$\leq 4.0 \times 10^3$ ^{c)}

a) [pyrazine] = 1.3×10^{-4} M.

b) Values to $\pm 10\%$, obtained from an average of at least four concentrations.

c) Estimated value derived from the decay of ^3Pz in the neat solvents.

alcohols, was found to quench the pyrazine triplet very effectively. Quenching rate constants of 1.3×10^8 , 2.7×10^7 and 6.7×10^6 M⁻¹sec⁻¹ for isopropyl alcohol, methyl alcohol and *tert*-butyl alcohol, respectively, were derived. This observation supports the $^3(n, \pi^*)$ assignment given previously [3]. It is important to note that these quenching rates are ≈ 100 times greater than the corresponding rates for quenching of $^3(n, \pi^*)$ excited states of phenones and related aromatic carbonyl compounds [9]. Thus, the $^3(n, \pi^*)$ of diazines appear to be considerably more electrophilic than the $^3(n, \pi^*)$ of aromatic carbonyl compounds.

On laser photolysis of pyrazine in neat acetonitrile, the ^3Pz decays with $k = 7.2 \times 10^4$ sec⁻¹. In neat cyclohexane, the ^3Pz is relatively short-lived with $k \approx 9.0 \times 10^7$ sec⁻¹. In neat isopropyl alcohol, the ^3Pz is too short-lived to be observed under our time resolution. Quenching of the $^3(n, \pi^*)$ state takes place, though one cannot exclude the possibility that some of the $^1(n, \pi^*)$ state may also have been quenched by isopropyl alcohol and cyclohexane.

4. Chemistry of $^3(n, \pi^*)$ pyrazine

Quenching of the triplet state of pyrazine in aqueous solutions by H-atom donors was found to produce new transient absorptions. Laser photolysis of 1.0×10^{-4} M pyrazine in the presence of 2.0 M isopropyl alcohol at

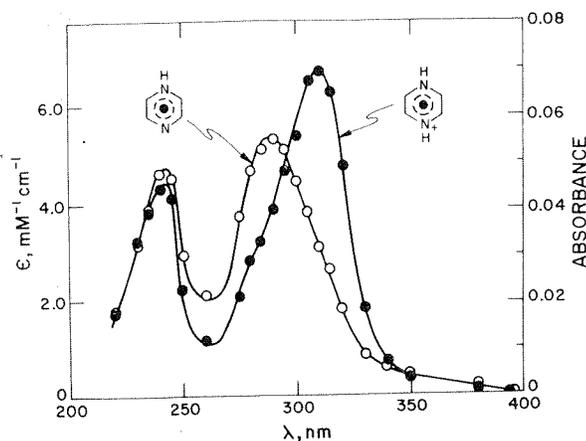
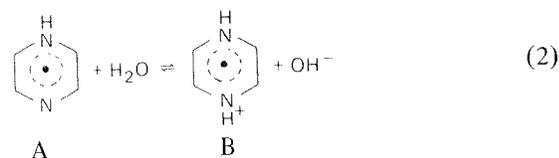
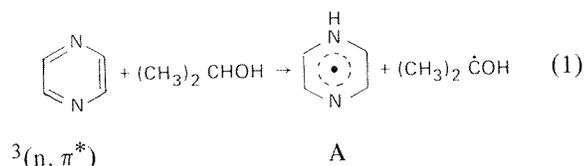


Fig. 2. Absorption spectra of the radicals produced on quenching of the triplet state of pyrazine by an H-atom donor: argon-saturated aqueous solutions of 1.3×10^{-4} M pyrazine and 2.0 M isopropyl alcohol at pH 6.4 (10^{-4} M phosphate buffer). Absorbances read at ≈ 30 nsec (\circ) and at ≈ 1.0 μ sec (\bullet).

pH 6.4 (argon-saturated solution) gave rise during the pulse to a transient spectrum (A) with maxima at 290 and 242 nm, see fig. 2. The spectrum (B) observed at ≈ 1.0 μ sec after the pulse gave bands with maxima at 310 and 242 nm. These optical spectra are identical to the ones recently observed [7] in the pulse radiolysis of pyrazine in water, and are assigned to the neutral radical and the dihydro radical cation of pyrazine, respectively.

The chemical reaction of $^3(n, \pi^*)$ pyrazine is suggested to be as follows:



The acetone ketyl radical does not react with pyrazine to form a second molecule of A since the redox potentials for such a reaction are not favourable [7, 10]. Instead, the $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ radical decays by second-order kinetics [7, 11]. The rate of protonation of radical A

to form radical B has been monitored at 290 nm and 310 nm and a $k \approx 7.0 \times 10^6 \text{ sec}^{-1}$ has been found in 0.5 M isopropyl alcohol at pH = 7.1. Assuming that this protonation is by water, a $k \approx 1.3 \times 10^5 \text{ M}^{-1}\text{sec}^{-1}$ can be derived for reaction (2). The ionization constant of radical B was found [7] to be 10.6. Support for these assignments was derived from ESR studies [12–14].

It is important to point out that the quenching of ^3Pz by isopropyl alcohol apparently does not occur via an electron transfer from the alcohol since the Pz^- radical anion ($\lambda_{\text{max}} = 340 \text{ nm}$ [7]) was not observed at $\approx 20 \text{ nsec}$ time resolution (details of experimental conditions will be presented elsewhere [8]).

Based on the extinction coefficient of radical B ($\epsilon_{310} = 6.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$) obtained by pulse radiolysis [7], the extinction coefficient of the T–T absorption spectrum of pyrazine was derived. This was based on the assumption that quenching of the $^3(n, \pi^*)$ state by isopropyl alcohol produced stoichiometric equivalents of radicals A and B.

Laser photolysis of pyrazine in neat cyclohexane gave a transient spectrum which can be assigned to the superposition of the optical spectrum of radical A and that of the cyclohexyl $\text{C}_6\text{H}_{11}^\bullet$ radical (previously determined [15]).

Similar observations have been found for the $^3(n, \pi^*)$ of pyrimidine. Quinoxaline has a $^3(\pi, \pi^*)$ as its lowest triplet state [5], and a much slower quenching by H-atom donors was observed. These and other results will be published in detail [8].

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